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A SYSTEMATIC HANDBOOK
OF
VOLUMETRIC ANALYSIS.



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A
SYSTEMATIC HANDBOOK
OF
VOLUMETRIC ANALYSIS;
OR,
THE QUANTITATIVE ESTIMATION
OF CHEMICAL SUBSTANCES BY MEASURE, APPLIED TO
LIQUIDS, SOLIDS, AND GASES.

ADAPTED TO THE REQUIREMENTS OF PURE CHEMICAL RESEARCH, PATHOLOGICAL
CHEMISTRY, PHARMACY, METALLURGY, MANUFACTURING
CHEMISTRY, PHOTOGRAPHY, ETC., AND FOR THE VALUATION OF SUBSTANCES
USED IN COMMERCE, AGRICULTURE, AND THE ARTS.

BY
FRANCIS SUTTON, F.C.S.
NORWICH.

SECOND EDITION.



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PREFACE TO THE SECOND EDITION.

SEVEN years have passed since the first edition of this book was published, and during that time considerable changes have occurred in theoretical chemistry, and some advance has undoubtedly been made in the practical application of modern views to chemical analysis in general. There is perhaps nothing very new or startling in volumetric analysis, but it has had its share of the general progress, and is evidently extending in application and usefulness notwithstanding a strong prejudice against its newer developments shown by some of the older school of operators

A larger acquaintance with the subject has convinced me that, although the saving of time and labour as against gravimetric analysis is very considerable, yet it necessitates a more thorough experimental knowledge of the re-action of bodies upon each other. Many a process has been thrown over in haste as being useless when a little patient and careful observation of its details would have resulted in a different opinion of its merits.

The modern system of atomic weights has been adopted in the present edition, but the alteration is in many cases merely a nominal one, since the systematic arrangement previously in vogue facilitates the calculation of results, and needs in no

way to interfere with the theory of the chemical constitution of bodies. The present edition is considerably enlarged by the extension of the sections on analysis of gases.

For the description of apparatus and the processes for water analysis contained in §§ 82, 83, and 84, I am indebted to Mr W. Thorp, F.C.S., principal assistant chemist to the Royal Commission on the Pollution of Rivers, who is constantly employed in the practical working of the methods described. Dr Frankland has also very kindly given some valuable suggestions. Clark's process for softening water has been copied from a form issued by the Rivers Commission.

The part devoted to analysis of gases has been contributed by Mr Herbert M^cLeod, F.C.S., late of the Royal College of Chemistry, and now Professor of Chemistry and Experimental Science at the Indian Civil Engineering College, whose practical acquaintance with the subject is well known. The very admirable original drawings furnished for the part by Professor M^cLeod, and which have been copied in the wood engravings, are worthy of especial notice. To these gentlemen I tender my sincere thanks.

FRANCIS SUTTON.

NORWICH, *September* 1871.

PREFACE TO THE FIRST EDITION.

THE rapid strides in all branches of industrial science and art during the last ten or fifteen years have, in a great measure, been aided, if not instigated, by chemical knowledge; and not the least important part of this knowledge relates to chemical analysis, or the determination of the nature, constitution, or economic value of various agents and products used in, or resulting from, manufacturing processes.

The same remark applies, also, to certain branches of the fine arts, together with medicine, pharmacy, agriculture, and general commerce, so that practical chemistry has become a thing of general need in technology. Under these circumstances, therefore, it is not surprising that the energies of scientific men have been taxed to devise new and rapid methods of chemical analysis to meet the wants of these high-pressure times; and such a branch has been developed in volumetric analysis, by which a large amount of time, labour, and therefore cost has been saved, as compared with the older methods of research.

Some idea of the extent to which this system has grown may be obtained by a glance at the following pages, which are devoted, not to a history of all the processes that have been devised and advocated, but exclusively to those which have been well tried and found worthy of confidence; for, like all new branches of science, volumetric analysis has had an abundant crop of weeds and rubbish, together with, here and there, sound fruit.

It is not to the labours of English chemists, however, that

this department of practical chemistry is indebted for its main growth, but to those of Germany and France, who appear to have recognised more readily than ourselves the value of the system.

In proof of this we have only to remember the names of Gay Lussac, Descroillez, Liebig, Bunsen, and Mohr, who have been the founders of it; nevertheless, the services rendered to it by our own countrymen—Faraday, Penny, Ure, Griffin, and others, are by no means contemptible.

Up to the present time, with the exception of a small and somewhat exclusive book,* written by Mr Scott, of the Trinity Office, Dublin, there has been no English text-book on the subject; the want of this has been felt, and often expressed. I trust I shall not be thought presumptuous in hoping that this treatise will supply that want. The experiments, made in connection with the various processes for the purpose of testing their accuracy, have extended over several years, and amounted in number to many thousands. The book is, therefore, based on the right foundation, granting only (and this is of the utmost importance) that the foundation be rightly laid. Very little will be found in it in the way of originality or personal discovery, for I hold to the doctrine advanced by the wisest of men, that “in the multitude of counsellors there is safety,” and consequently have adhered mainly to those processes which have received the approval of general experience. Nevertheless, I trust, that whatever is new in system or arrangement may find a generous reception.

The necessities of the present day require that analytical investigations should be directed into many channels hitherto open only to the purely scientific chemist, but I doubt not that the introduction of the simpler and more expeditious methods of determination comprised in volumetric analysis, will, in some measure, put it within the power of the educated pharmaceutical chemist or chemical manufacturer to exercise his power, either for his own or others' benefit, and thus leave the man of science to follow the higher paths of that vast territory yet open to genius.

The student and the uninitiated must not, however, imagine

* Longmans.

that the possession of this or any other book of its class will put him into a royal road to chemical analysis. The only real method of progress is that which is gained by honest and truthful practice, beside which, to make the best and most reliable use of the system, the operator must possess a good knowledge of the laws of chemical combination and decomposition, so as to know where he may apply any of the processes here given with security. Had the book been written with a view to provide this necessary knowledge, it must have been a work of much larger dimensions, and would then probably not have been so useful as many books already in existence, devoted to general chemistry and the principles of analysis; among which the student who desires this preliminary knowledge, cannot do better than consult Fownes' "Manual of Chemistry;" Abel and Bloxam's "Handbook of Chemistry;" Miller's "Elements of Chemistry;" and the latest editions of Fresenius' "Qualitative and Quantitative Analysis."

The main feature of volumetry is not so much analysis, in the proper sense of the term, as the quantitative determination of one principal constituent of a substance, and in many cases of this kind the accuracy obtained by an ordinarily careful operator, such as in alkalimetry, for example, leaves nothing to be desired; while under other circumstances, such as the estimation of one particular metal in solution containing other metallic compounds, the operation may require the exercise of much more judgment and skill. I have endeavoured to provide, as far as possible, for these difficulties, by special explanations.

The matter contained in Part V. (now Part VI.) is an attempt to make the volumetric system of examination complete and exhaustive, so far as certain substances are concerned, and though not in every case such as I should, *by preference*, use in my own laboratory, yet I believe will be found worthy of confidence. The value of this department consists, mainly, in the fact that the determinations can mostly be made with simple and inexpensive apparatus, and are within the reach of any well-informed medical man or pharmaceutical chemist; the latter of whom, in provincial districts, ought to be able to estimate the value of a sample

of alkali, bleaching powder, or manganese, or determine the principal constituents of water, urine, manures, or soils, when called upon to do so.

The section on the analysis of urine includes the estimation of almost every constituent likely to be required, and though written as concisely as possible, I hope it will be found suitable to the wants of the medical student.

No pains have been spared, either on my own or the printer's part, to render the book thoroughly accurate; but in a book of this character, containing so many figures and technical expressions, it is a thing of no small difficulty; especially if it be considered that the only time at my disposal for either writing or revising the book, has been at the beginning or close of a full day's work; nevertheless, I trust that whatever errors may yet be found will be of minor importance.

FRANCIS SUTTON.

NORWICH, *January* 1863.



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Names of Elementary Substances of Ordinary Occurrence, with their Symbols and Atomic Weights, as given by the latest and best Authorities.

NAME.	SYMBOL.	ATOMIC WEIGHT.
Aluminium,	Al	27·5
Antimony,	Sb	122
Arsenic,	As	75
Barium,	Ba	137
Bismuth,	Bi	210
Boron,	B	11
Bromine,	Br	80
Cadmium,	Cd	112
Calcium,	Ca	40
Carbon,	C	12
Chlorine,	Cl	35·5
Chromium,	Cr	52·5
Cobalt,	Co	58·5
Copper,	Cu	63·5
Fluorine,	Fl	19
Gold,	Au	196·5
Hydrogen,	H	1
Iodine,	I	127
Iron,	Fe	56
Lead,	Pb	207
Lithium,	Li	7
Magnesium,	Mg	24
Manganese,	Mn	55
Mercury,	Hg	200
Molybdenum,	Mo	96
Nickel,	Ni	58·5
Nitrogen,	N	14
Oxygen,	O	16
Palladium,	Pd	106·5
Phosphorus,	P	31
Platinum,	Pt	197
Potassium,	K	39
Silicon,	Si	28
Silver,	Ag	108
Sodium,	Na	23
Strontium,	Sr	87·5
Sulphur,	S	32
Tin,	Sn	118
Uranium,	Ur	120
Zinc,	Zn	65

Abbreviations and Explanations.

The atomic weights used are based on the latest researches.

The formulæ are constructed on the basis $H = 1$. $O = 16$.
 $H^2O = 18$.

The normal temperature for the preparation and use of standard solutions is $16^\circ C.$, or about 60° Fahr.

c.c. denotes cubic centimetre.

gm. „ gramme = 15.43235 grains English.

grn. „ grain.

dm. „ decem = 10 fluid grains.

1 Litre = 1000 c.c.

1 c.c. = 1 gm. distilled water at $16^\circ C.$

1 dm. = 10 grn. „ „ „

Distilled water is to be used in all the processes, unless otherwise expressed.

Normal Solutions are those which contain one gramme atom of re-agent (taken as monobasic), or an equivalent in some active constituent (*e.g.* oxygen) in the litre.

Decinormal Solutions are one-tenth of that strength = $\frac{N}{10}$.

Centinormal, one-hundredth = $\frac{N}{100}$.

Empirical Standard Solutions are those which contain no exact atomic proportion of re-agent, but are constructed generally so that 1 c.c. = 0.01 gm. (one centigramme) of the substance sought.

A Titrated Solution (from the French word *titre*, title or power) denotes a solution whose strength or chemical power has been accurately found by experiment.

When a chemical substance or solution is directed to be *titrated*, the meaning is that it is to be quantitatively tested for the amount of pure substance it contains by the help of standard or titrated solutions. The term is used in preference to *tested* or *analysed*, because these expressions may relate equally to qualitative and quantitative examinations, whereas titration can only apply to quantitative examination.

VOLUMETRIC ANALYSIS

OF

LIQUIDS AND SOLIDS.



PART I.

GENERAL PRINCIPLES.

§ 1. QUANTITATIVE analysis by weight, or gravimetric analysis, consists in separating out the constituents of any compound, either in a pure state or in the form of some new substance of known composition, and accurately weighing the products. Such operations are frequently very complicated, and occupy a long time, besides requiring in many cases elaborate apparatus, and the exercise of much care and experimental knowledge. Volumetric processes, on the other hand, are, as a rule, quickly performed; in most cases are susceptible of extreme accuracy, and need much simpler apparatus. The leading principle of the method consists in submitting the substance to be estimated to certain characteristic reactions, employing for such reactions solutions of known strength, and from the volume of solution necessary for the production of such reaction, determining the weight of the substance to be estimated by aid of the known laws of chemical equivalence.

Volumetric analysis, or quantitative chemical analysis by measure, in the case of liquids and solids, consequently depends upon the following conditions for its successful practice:—

1°. A solution of the re-agent or test, the chemical power of which is accurately known, called the “standard solution.”

2°. A graduated vessel from which portions of it may be accurately delivered, called the burette.

3°. The decomposition which the test solution produces with any given substance must be of such a character that its ter-

mination is unmistakable to the eye, and thereby the quantity of the substance with which it has combined accurately determined.

Suppose, for instance, that it is desirable to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form chloride of silver, which is insoluble in nitric acid. The proportions in which the combination takes place are 35·5 of chlorine to every 108 of silver; consequently if a standard solution of pure chloride of sodium is prepared by dissolving 58·5 grains of the salt (*i.e.*, 1 at. sodium 23, 1 at. chlorine 35·5 = 1 at. chloride of sodium, 58·5) in so much distilled water as will make up exactly 1000 grain measures; every single grain measure of this solution will combine with 0·108 grain of pure silver to form chloride of silver, which precipitates to the bottom of the vessel in which the mixture is made. In the process of adding the salt solution to the silver, drop by drop, a point is at last reached when the precipitate ceases to form. Here the process must stop. On looking carefully at the graduated vessel from which the standard solution has been used, the operator sees at once the number of grain measures which have been necessary to produce the complete decomposition. For example, suppose the quantity used was 520 grains; all that is necessary to be done is to multiply 520 by the coefficient for each grain measure, *viz.* 0·108, which shows the amount of pure silver present to be 56·16 grains.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the estimation by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which have not been described, those will be found in their proper place, but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; beside which, in the majority of instances in which it can be applied, it is equally accurate, in many cases much more so. For technical purposes, such as the examination of substances used in arts and manufactures, the system has been a great boon, and every day is bringing fresh applications of it both to pure and applied chemical science.

The only condition on which the volumetric system of analysis can be carried on successfully, is that the greatest care is exercised with respect to the graduation of the measuring instruments, and the strength and purity of the standard solutions. A very slight error in the analytical process becomes considerably magnified when calculated for pounds, hundredweights, or tons of the substance tested.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive vegetable colouring matter. The formation of a permanent precipitate, as in the estimation of cyanogen. A precipitate ceasing to form, as in chlorine and silver determinations. The appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by Mohr and others, namely:—

1. Where the determination of the substance is effected by saturation with another substance of opposite properties,—generally understood to include acids and alkalies.

2. Where the determination of a substance is effected by a reducing or oxidising agent of known power, including most metals, with their oxides and salts; the principal oxidising agents being potassic permanganate, potassic bichromate, and iodine; and the corresponding reducing agents, ferrous and stannous compounds, and sodic hyposulphite.

3. Where the determination of a substance is effected by precipitating it in some insoluble and definite combination, an example of which occurs in the estimation of silver described above.

This classification does not rigidly include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the reagents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be analysed under two or three heads; copper, for instance, can be determined residually by potassic permanganate; it can also be determined by precipitation with sodic sulphide. The estimation of the same metal by potassic cyanide, on the other hand, would not come under any of the heads.

It will be found, therefore, that liberties have been taken with the arrangement, and for convenient reference all analytical processes applicable to a given body are included under its name.

THE INSTRUMENTS AND APPARATUS.

THE BALANCE.

§ 2. STRICTLY speaking, it is necessary to have two balances in order to carry out the Volumetric System completely; one to carry about a kilogramme in each pan, and turn when loaded with about five milligrammes. This instrument is used for graduating flasks, or for testing them, and for weighing large amounts of pure reagents for standard solutions. The second balance should be light and delicate, to carry about fifty grammes, and turn easily and quickly when loaded with one or two-tenths of a milligramme. This instrument serves for weighing small quantities of substances to be tested, many of which are hygroscopic, and need to be weighed quickly and with great accuracy; it also serves for testing the accuracy of pipettes and burettes.

For all technical purposes, however, a moderate-sized balance of medium delicacy is quite sufficient, especially if rather large quantities of substances are weighed and brought into solution—then further subdivided by means of measuring-flasks and pipettes.

The operator also requires, beside the balance and the graduated instruments, a few beakers, porcelain basins, flasks, funnels, stirring-rods, &c., as in gravimetric analysis.

VOLUMETRIC ANALYSIS WITHOUT WEIGHTS.

§ 3. THIS is more a matter of curiosity than of value; but, nevertheless, one can imagine circumstances in which it might be useful. In carrying it out, it is necessary only to have (1) a correct balance, (2) a pure specimen of substance to use as a weight, (3) an accurate burette filled with the proper standard solution.

With a perfectly pure specimen of substance, say calcic carbonate, a normal acid will show, of course, 100 per cent. If, then, a pure specimen be put into one scale of the balance, and be counterpoised with an impure specimen of the same substance, and the latter titrated with normal acid, the number of c.c. used will be the percentage of pure calcic carbonate in the specimen.

The application of the process is, of course, limited to the use of such substances as are to be had pure, and whose weight is not variable by exposure; but where even a pure substance of one kind cannot be had as a weight, one of another kind may be used as a

substitute, and the required result obtained by calculation. For instance, it is required to ascertain the purity of a specimen of sodic carbonate, and only pure calcic carbonate is at hand to use as a weight, equal weights of the two are taken, and the impure specimen titrated with normal acid. To arrive at the required answer, it is necessary to find a coefficient or factor by which to convert the number of c.c. required by the sodic carbonate, weighed on the calcic, into that which should be required if weighed on the sodic basis. A consideration of the relative atomic weights of the two bodies will give the factor thus—

$$\frac{\text{Atomic weight calcic carbonate } 100}{\text{Atomic weight sodic carbonate } 106} = 0.9434.$$

If, therefore, the c.c. found are multiplied by this number, the percentage of pure sodic carbonate will be obtained. The method may be extended to a number of substances, on this principle, with the exercise of a little ingenuity.

VOLUMETRIC ANALYSIS WITHOUT BURETTES OR OTHER GRADUATED INSTRUMENTS.

§ 4. THIS operation consists in weighing the standard solutions on the balance instead of measuring them. The influence of variation in temperature is, of course, here of no consequence. The chief requisite is a delicate flask, fitted with tube and blowing ball, as in the burette, fig. 3, or an instrument known as Schuster's alkalimeter may be used. The method is capable of very accurate results, if care be taken in preparing the standard solutions and avoiding any loss in pouring the liquid from the vessel in which it is weighed.

THE BURETTE.

§ 5. THIS instrument is used for the delivery of an accurately-measured quantity of any particular standard solution. It invariably consists of a long glass tube of even bore, throughout the length of which are engraved, by means of hydrofluoric acid, certain divisions corresponding to a known volume of fluid.

It may be obtained in a great many forms, under the names of their respective inventors, such as Mohr, Gay Lussac, Binks, &c., but as some of these possess a decided superiority over others, it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The

burette, with india-rubber tube and clip, contrived by Dr Frederic Mohr of Bonn, shown in figs. 1 and 2, has the preference above all others for general purposes.

The advantages possessed by this instrument are, that its constant upright position enables the operator at once to read off the number of degrees of test solution used for any analysis. The quantity of

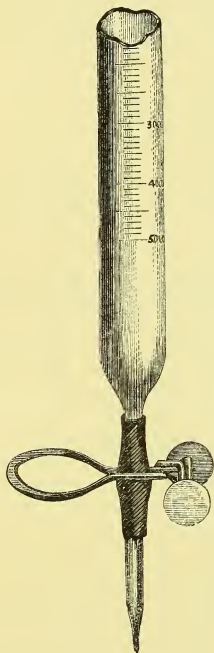


Fig. 1.

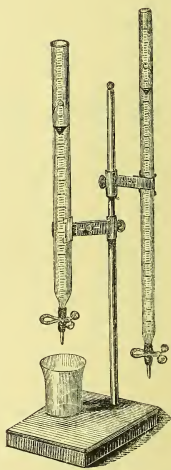


Fig. 2.

fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip, and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks' or Gay Lussac's

form of instrument. The principal disadvantage, however, of these two latter forms of burette is, that a correct reading can only be obtained by placing them in an upright position, and allowing the fluid to find its perfect level. The preference should therefore, unhesitatingly, be given to Mohr's burette, wherever it can be used; the greatest drawback to it is, that it cannot be used for permanganate in consequence of its india-rubber tube, which decom-

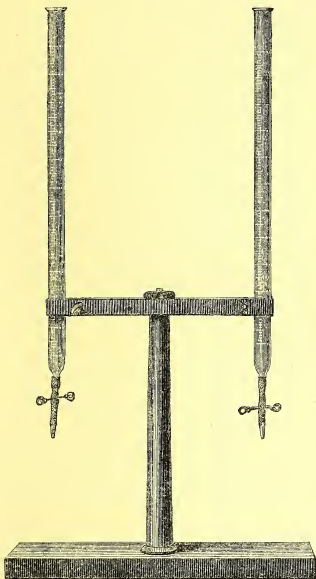


Fig. 3.

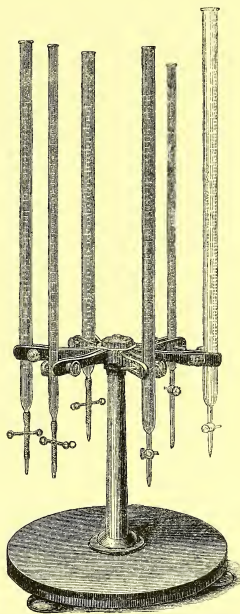


Fig. 4.

poses the solution. This, however, can be entirely obviated by the use of the same kind of burette fitted with a delicate glass stop-cock, as shown in fig. 4. This tap burette, if made in a proper manner, is very serviceable, as it can be used not only for permanganate solution, but all others except caustic alkalies, and may also be arranged so as to deliver the solution in drops, leaving both the

hands of the operator disengaged. The tap should be ground very accurately, and the end of the plug should have a collar of india-rubber or buckskin fastened on it, so as to prevent the tap from slipping out of its place. Owing to the action of caustic alkalis upon glass, such a burette does not answer well for solutions of potash or soda. Two convenient forms of stand for Mohr's burettes are shown in figs. 3 and 4; in the latter, the arms carrying the burettes revolve.

We are indebted to Mohr for another form of instrument to avoid the contact of permanganate and india-rubber, viz., the foot burette, with elastic ball, shown in fig. 5.

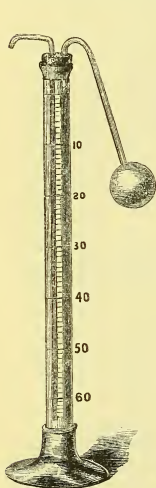


Fig. 5.

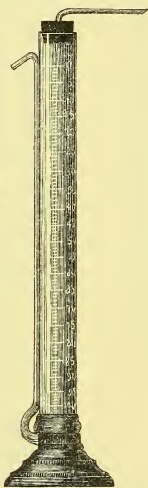


Fig. 6.

The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the ball, which should be large, and have two openings,—one cemented to the tube with marine glue, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills itself with air.

Gay Lussac's burette, supported in a wooden foot, may be used instead of the above form, by inserting a good fitting cork into the open end, through which a small tube bent at right angles is passed. If the burette is held in the right hand, slightly inclined to-

wards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in an horizontal position, to the great danger of spilling the contents, is avoided; at the same time, the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation more accurately determined.

Fig. 6 will show the arrangement here described.

There is an arrangement of Mohr's burette which is extremely serviceable, when a constant series of analyses of the same character have to be made, such as in alkali works, assay offices, &c. It consists in having a T piece of glass tube inserted between the lower end of the burette and the spring clip, which communicates with a reservoir of the standard solution, placed above, so that the burette

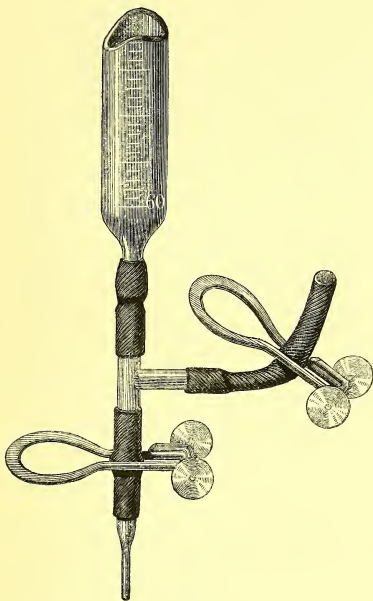


Fig. 7.

may be filled as often as emptied, by a syphon, and in so gradual a manner that no air bubbles occur, as in the case of filling it with a funnel, or pouring in liquid from a bottle; beside which, this plan prevents evaporation or dust in the standard solution either in the burette or reservoir; it is especially applicable to burettes containing caustic alkalies.

Figs. 7 and 8 show the arrangement in detail.

It sometimes happens that a solution requires titration at a hot or even boiling temperature ; in which case the ordinary arrangement of Mohr's burette will not be available since the steam rising from the liquid heats the burette and alters the volume of

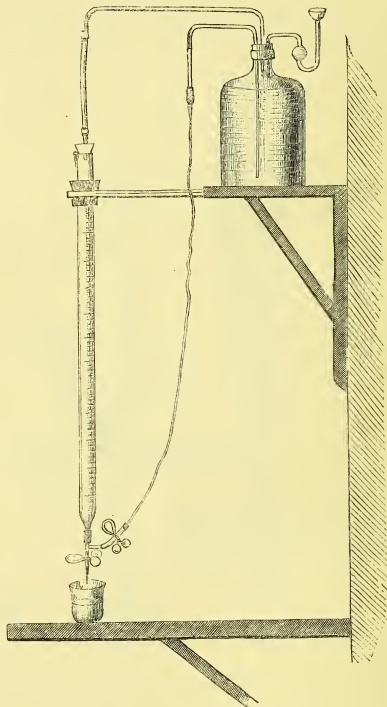


Fig. 8.

fluid. This may be avoided by using a much longer piece of india-rubber tube, so that the burette stands at the side of the capsule or beaker being heated, and the elastic tube is brought over its edge ; the pinch-cock is fixed midway ; no heat can then reach the body of fluid in the burette, since there can be no conduction past the pinch-

cock ; if this plan is not adopted, a Gay Lussac or ball burette should be used.

Gay Lussac's burette, shown in fig. 9, should have a wooden support or foot into which it may be inserted, so as to be read correctly. By using it in the following manner, its natural disadvantages may be overcome to a great extent. Having fixed the burette into the foot securely, and filled it, take it up by the foot with the left hand, and resting the upper end upon the edge of the beaker into which the solution to be tested is placed, drop the test fluid from the burette, meanwhile stirring the contents of the beaker with a glass rod held in the right hand ; by a slight elevation or depression of the left hand, the flow of test liquid is regulated until the end of the operation is secured, thus avoiding the annoyances which arise from alternately placing the instrument in an upright and horizontal position.

Geissler's burette differs from Gay Lussac's in having the fine tube enclosed within the large one, but as it is a difficult instrument to make, it has not found much favour.

Binks', or, as it is sometimes called, the English



Fig. 9.

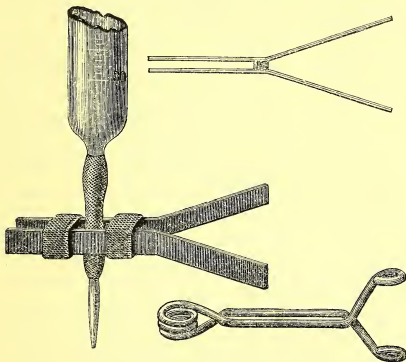


Fig. 10.

burette, is well known, and need not be described ; it is the least recommendable of all forms.

It is most convenient to have burettes graduated to 25 or 30 c.c. in $\frac{1}{10}$, 55 or 60 c.c. in $\frac{1}{2}$, and 100 or 110 c.c. in $\frac{1}{4}$.

The kind of pinch-cock (quetschhahn) generally used in Mohr's burette is shown in fig. 1. These are made of brass and soldered, which is an objection, as they frequently come to pieces under the action of the solutions. I have for some time used pinch-

cocks made of one piece of steel wire, as devised by Hart; the wire is softened by heating and coiled round, as shown in fig. 10.

When the proper shape has been attained the clip is hardened and tempered so as to convert it into a spring.

Another useful pinch-cock is shown in fig. 10. It may be made of hard-wood, horn, or, preferably, of flat glass rod. The levers should be long. A small piece of cork, of the same thickness as the elastic tube of the burette when pressed close, should be fastened at the angles of the levers as shown in the engraving.

THE PIPETTE.

§ 6. THE pipettes used in volumetric analysis are of two kinds, viz., those which deliver one certain quantity only, and those which are graduated on the stem, so as to deliver various quantities at the discretion of the analyst. In the former kind, or whole pipette, the graduation may be either that in which the fluid is suffered to run out by its own momentum or in which it is blown

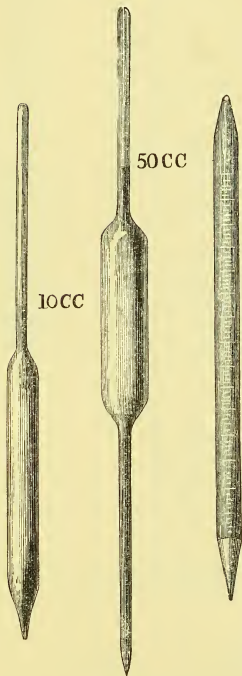


Fig. 11.

out by the breath. The best form is that in which the liquid flows out by its own momentum, but in this case the last few drops empty themselves very slowly, but if the lower end of the pipette be touched against the moistened edge of the beaker or other vessel into which the fluid is poured, the flow is hastened considerably,

and in graduating the pipette, it is preferable to do it on this plan.

In both the whole and graduated pipettes, the upper end is narrowed to about $\frac{1}{8}$ inch, so that the pressure of the moistened finger is sufficient to arrest the flow at any point.

Fig. 11 shows two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size. It must be borne in mind that the pipette graduated throughout the stem is not a reliable instrument for actual analysis, owing to the difficulty of stopping the flow of liquid at any exact point and reading off the exact measurement. Its chief use is in the approximate estimation of the strength of any standard solution in the course of preparation.

THE MEASURING FLASKS.

§ 7. THESE indispensable instruments are made of various capacities; they serve to mix up standard solutions to a given volume, and also for the subdivision of the substance to be tested by means of the pipettes, and are in many ways most convenient. They should be tolerably wide at the mouth, and have a well-ground glass stopper, and the graduation line should fall just below the middle of the neck, so as to allow room for shaking up the fluid. Convenient sizes are 100 c.c. (to deliver), 100, 200, 250, 300, 500, and 1000 c.c., the latter all graduated to *contain* the respective quantities. A litre flask is shown in fig. 12.

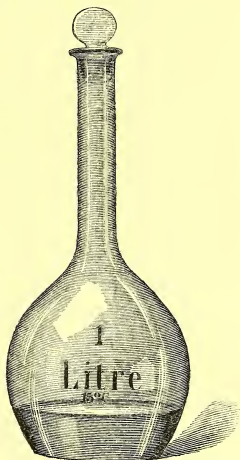


Fig. 12.

ON THE CORRECT READING OF GRADUATED INSTRUMENTS.

§ 8. THE surface of liquids contained in narrow tubes is always curved, in consequence of the capillary attraction exerted by the

sides of the tube, and consequently there is a difficulty in obtaining a distinct level in the fluid to be measured. If, however, the lowest point of the curve is made to coincide with the graduation

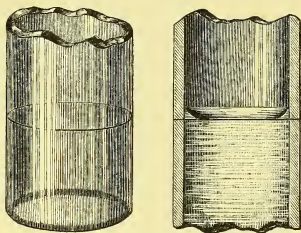


Fig. 13.

mark, a correct proportional reading is always obtained, hence this method of reading is the most satisfactory ; see fig. 13.

The eye may be assisted materially in reading the divisions on a graduated tube by using a small card, the lower half of which is blackened, the upper remaining white. If the line of division between the black and white be held about an eighth of an inch below the surface of the liquid, and the eye brought on a level with it, the meniscus then can be seen by transmitted light, bounded below by a sharply defined black line. A card of this kind, sliding up and down a support, is of great use in verifying the graduation of the burettes or pipettes with a cathetometer. The burette or pipette is filled with water at the proper temperature, and the contents of each division of 10 c.c. or so carefully read off with the telescope and weighed. In order to do this with pipettes they must be fixed in a burette support, and have over their upper end a tightly fitting elastic tube closed with a pinch-cock. The operator may here consult with advantage the details of graduating and verifying measuring instruments for the analysis of gases as described in Part 7.



Fig. 14.

Erdmann has contrived a useful little instrument to accompany Mohr's burette, which gives the most accurate reading that can be obtained ; its form is shown in fig. 14, and is known by the name of Erdmann's float. It consists of an elongated glass bulb, rather smaller in diameter than the burette itself, and is weighted at the lower end with a globule of mercury, like an hydrometer. It is drawn to a point at the upper end, and the point is bent round so as to form a small hook, by means of which it can be lifted in and out of the burette with a bent wire ; a line is made with a diamond round its middle by

means of a lathe, and the coincidence of this line with the graduation mark of the burette is accepted as the true reading. The actual height of the liquid in the burette is not regarded, because if the operator begins with the line on the float, opposite the 0 graduation mark on the burette, the same proportional division is always maintained.

It is essential that the float should move up and down in the burette without wavering, and the circle upon it should always be parallel to the graduations of the burette. One great value of this float is found in testing the accuracy of the burette itself ; it enables a strict comparison to be made between say each 10 c.c., with very slight differences in weighing, supposing the instrument to be correct. It is always well, however, to bear in mind that absolute accuracy cannot be obtained in graduating instruments ; 5 or 10 milligrammes either way in 10 c.c. may safely be disregarded.

To prevent evaporation and the entrance of dust in Mohr's burette, the inventor recommends a well polished marble, such as boys play with, to be laid on the open end. In burettes containing caustic alkaline solutions, a cork with carbonic acid tube should be used if the solution is allowed to remain in them for any length of time.

Besides the measuring flasks it is necessary to have graduated vessels of cylindrical form, for the purpose of preparing standard solutions, &c.

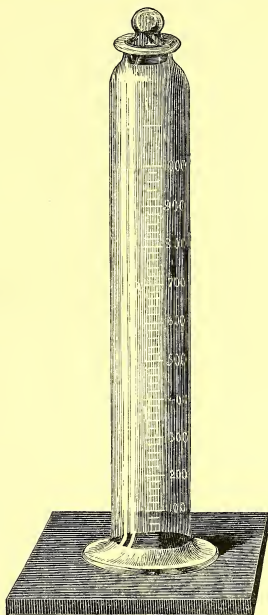


Fig. 15.

Fig. 15 shows a stoppered cylinder for this purpose, generally called a test mixer.

**ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE
ADOPTED IN VOLUMETRIC ANALYSIS.**

§ 9. It is much to be regretted that the decimal system of weights and measures used on the Continent is not universally adopted, for scientific and medicinal purposes, in England. Its great advantage is its uniformity throughout. The unit of weight is the gramme ($= 15.43235$ grains troy), and a gramme of distilled water at 4° C. or 39° Fahr., measures exactly a cubic centimètre. The kilogramme contains 1000 grammes. The litre 1000 cubic centimètres.

It may not be out of place here to give a short description of the origin of the French decimal system, now used exclusively for scientific purposes in that country, and also in Prussia, Austria, Holland, Sweden, Denmark, Belgium, and Spain.

The commission appointed in France for the purpose of instituting a decimal system of weights and measures, founded their standard on the length of the meridian arc between the pole and equator, the ten-millionth part of which was called the mètre ($= 39.3710$ English inches), although the accuracy of this measurement has been disputed. It would have been preferable, as since proposed, that the length of a pendulum vibrating exactly 86,400 times in twenty-four hours, or one second for each vibration, equivalent to 39.1372 English inches, should have been taken as the standard mètre, in which case it would have been much easier to verify the standard in case it should be damaged or destroyed. However, the actual mètre in use is equal to 39.371 inches, and from this standard its multiples and subdivisions all proceed decimally, its one-tenth part being the decimètre, one hundredth the centimètre, and one thousandth the millimètre.

In accordance with this, a cube of distilled water at its greatest density, viz., 4° C., or 39° Fahr., whose side measures one decimètre, has exactly the weight of one kilogramme, or 1000 grammes, and occupies the volume of 1 litre, or 1000 cubic centimètres.

This simple relationship between liquids and solids is of great value in a system of volumetric analysis, and even for ordinary analysis by weight; for technical purposes it is equally as applicable as the grain system, the results being invariably tabulated in percentages. Complete tables of these weights and measures will be found at the end of the book.

With these brief explanations, therefore, I have only to state that the French decimal system will be mainly used throughout this treatise, but at the same time those who may desire to adhere to the ordinary grain weights, can do so without interfering with the accuracy of the processes described.

As has been before stated, the true cubic centimeter contains one gramme of distilled water at its greatest density, viz., 4° C., or 39° Fahr.; but as this is a degree of temperature which it is impossible to work at for more than a month or two in the year, it is better to take the temperature of 16° C., or about 60° Fahr., as the standard, because in winter most laboratories or rooms have furnaces or other means of warmth, and in summer the same localities would not, under ordinary circumstances, have a much higher degree of heat than 16° C. In order, therefore, that the graduation of instruments on the metrical system may be as uniform as possible with our own fluid measures, the cubic centimeter should contain one gramme of distilled water at 16° C. The true c.c. (*i.e.*, = 1 gm. at 4° C., or 39° Fahr.) contains only 0.999 gm. (strictly 998,981) at that temperature; but for convenience of working, and for uniformity with our own standards of volume, it is better to make the c.c. contain one gramme at 16° C. The real difference is one-thousandth part. The operator, therefore, supposing he desires to graduate his own measuring flasks, must weigh into them 250, 500, or 1000 grammes of distilled water at 16° C., or 60° Fahr.

Fresenius and others have advocated the use of the strict litre by the graduation of instruments, so that the litre shall contain 999 gm. at 16° C. Mohr, on the contrary, uses 1000 gm., at the temperature of 17.5° , the real difference being 1.2 c.c. in the litre, or about one-eight hundredth part.

It will be seen above that I have advocated a middle course on two grounds—1st, That in testing instruments it is much easier to verify them by means of round numbers, such as 5 or 10 gm.; 2d, That there are many thousands of instruments already in use, varying between the two extremes, and as these cannot well be annihilated, the adoption of a mean will give a less probable amount of error between the respective instruments; and, moreover, the difference between the litre at 4° and 16° being one-thousandth part, it is easy to correct the measurement for the exact litre.

It matters not which plan is followed, if all the instruments in a particular set coincide with each other; but it would be manifestly wrong to use one of Mohr's burettes with one of Fresenius'

measuring flasks. Operators can, however, without much difficulty, re-mark their measuring flasks to agree with their smaller graduated instruments, if they are found to differ to any extent.

In the preparation of standard solutions, one thing must especially be borne in mind, namely, that saline substances on being dissolved in water have a considerable effect upon the volume of the resulting liquid. The same is also the case in mixing solutions of various salts or acids with each other. (See Gerlach, "Specifische Gewichte der Salzlösungen;" also Gerlach, "Sp. Gewichte von wässrigen Lösungen Zeitschrift für An. Chem.," vol. viii. p. 245.)

In the case of strong solutions, the condensation in volume is as a rule considerable; and, therefore, in preparing such solutions for volumetric analysis, or in diluting such solutions to a given volume for the purpose of removing aliquot portions subsequently for examination, sufficient time must be given for liquids to assume their constant volume at the standard temperature. If the strength of a standard solution is known for one temperature, the strength corresponding to another temperature can only be calculated if the rate of expansion by heat of the liquid is known. The variation cannot be estimated by the known rule of expansion in distilled water; for Gerlach has shown that even weak solutions of acids and salts expand far more than water for certain increments of temperature. The rate of expansion for pure water is known, and may be used for the purpose of verifying the graduation of instruments, where extreme accuracy is required. The following short table furnishes the data for correction. (See also Dittmar, "Watt's Chem. Dict.," p. 256.)

The weight of 1000 c.c. of water of t° C., when determined by means of brass weights in air of t° C., and at 0.76 m.m., is equal to $1000 - x$ gm.

t°	10	11	12	13	14	15	16	17	18	19	20
x	1.34	1.43	1.52	1.63	1.76	1.89	2.04	2.2	2.37	2.55	2.74
t°	21	22	23	24	25	26	27	28	29	30	
x	2.95	3.17	3.39	3.63	3.88	4.13	4.39	4.67	4.94	5.24	

Slight variations of atmospheric pressure may be entirely disregarded.

Bearing the foregoing remarks in mind, therefore, the safest plan

in the operations of volumetric analysis, so far as measurement is concerned, is to use solutions as dilute as possible. Absolute accuracy in estimating the strength of standard solutions can only be secured by weight, the ratio of the weight of the solution to the weight of active substance in it being independent of temperature.

The accurate graduation of burettes and pipettes can only be done by carefully constructed machines, and is, therefore, generally speaking, beyond the compass of the analyst himself; nevertheless, they should be carefully tested by him before being used, as, unfortunately, they do not always possess the accurate measurement to which they pretend. In the verification of both burettes and pipettes, it is only necessary to allow ten cubic centimeters of distilled water to flow into a dry and accurately tared flask or beaker. If the weight at 16° C., or 60° Fahr., is 10 grammes, it is sufficient; the next 10 grammes may be tried in like manner, and so on until the entire capacity is proved; differences of 5 or 10 milligrammes may be disregarded.

Beside the litre flask, it is advisable to have flasks graduated for 100, 200, 250, 300, and 500 c.c., as they are extremely serviceable in dividing small quantities of substance into still smaller proportional parts. Suppose, for instance, it is desired to take the tenth part of a solution for the purpose of separating any single constituent, let it be put into a 200 c.c. flask, and filled to the mark with water, and well shaken; 20 c.c. taken out with a pipette will at once give the quantity required.

Burettes, pipettes, and flasks may also be graduated in grains, in which case it is best to take 10,000 grains as the standard of measurement. In order to lessen the number of figures used in the grain system, so far as liquid measures are concerned, I propose that ten fluid grains be called a decem, or for shortness dm.; this term corresponds to the cubic centimeter, bearing the same proportion to the 10,000 grain measure as the cubic centimeter does to the litre, namely, the one-thousandth part. The use of a term like this will serve to prevent the number of figures, which are unavoidably introduced, by a small unit like the grain.

Its utility is principally apparent in the analysis for percentages, particulars of which will be found hereafter.

The 1000 grain burette or pipette will, therefore, contain 100 decems, the 10,000 gr. measure, 1000 dm., and so on.

The capacities of the various instruments graduated on the grain system may be as follows:—

Flasks 10,000, 5000, 2500, and 1000 grs., = 1000, 500, 250, and 100 dm. Burettes 300 grs. in 1 gr. divisions, for very delicate purposes = 30 dm. in $\frac{1}{10}$; 600 grs. in 2-gr. divisions, or $\frac{1}{2}$ dm.; 1100 grs. in 5-gr. divisions, or $\frac{1}{2}$ dm.; 1100 grs. in 10-gr. divisions, or 1 dm. The burettes are graduated above the 500 or 1000 grs., in order to allow of analyses for percentages by the residual method. Whole pipettes to deliver 10, 20, 50, 100, 200, 500, and 1000 grs.; graduated ditto, 100 gr. in $\frac{1}{10}$ dm.; 500 grs. in $\frac{1}{2}$ dm.; 1000 grs. in 1 dm.

Those who may desire to use the decimal systems constructed on the gallon measure = 70,000 grains, will bear in mind that the "septem" of Mr Griffin, or the "decimillem" of Mr Acland, are each equal to 7 grs., and therefore bear the same relation to the pound = 7000 grs., as the cubic centimeter does to the litre, or the decem to the 10,000 grs. An entirely different set of tables for calculations, &c., is required for these systems, but the analyst may readily construct them when once the principles contained in this treatise are understood.

VOLUMETRIC ANALYSIS ON THE ATOMIC SYSTEM AND THE PREPARATION OF NORMAL TITRATED SOLUTIONS.

§ 10. WHEN analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special re-agent, and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry a distinct standard acid was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions.

Griffin and Ure appear to have been the first to suggest the use of standard test solutions based on the atomic system, and following in their steps, Mohr has worked out a most elaborate and extensive system of analysis, which must be an inestimable boon to all who concern themselves with scientific and especially technical chemistry. Not only has Mohr done this, but in addition to it, has enriched his processes with so many original investigations, and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

His "Lehrbüch der Chemisch Analytischen Titirmethode," is the most complete treatise on the subject, and well deserving the thanks of all students of the science.

But to return to the explanation of the system, the normal standard solutions are so prepared as to contain either the half or the whole of the atomic weight of the required reagent weighed in grammes per litre.

In the case of reagents of a bivalent character, such as crystallised oxalic acid, for instance, the formula of which is $C^2O^4H^2$, $2H^2O = 126$, half its atomic weight = 63 gm., is dissolved in water so as to make up exactly a litre at $16^\circ C$. This constitutes the normal solution of oxalic acid used in alkalimetry.

Each c.c. of this solution will contain $\frac{1}{20000}$ of the atomic weight of oxalic acid in grammes, or $\frac{1}{2}$ milligramme atom = 0.063 gm., and will neutralise $\frac{1}{20000}$ of the atomic weight, or $\frac{1}{2}$ milligramme atom of any alkaline monocarbonate, *e.g.*, sodic monocarbonate 0.053 gm., or will combine with $\frac{1}{20000}$ of the atomic weight, or $\frac{1}{2}$ milligramme atom of a bivalent metal such as lead = 0.1035 gm.; 1 c.c. of the same normal solution will exactly saturate $\frac{1}{10000}$ of the atomic weight in grammes, or 1 milligramme atom of any caustic alkali, *e.g.*, potassic hydrate = 0.056 gm. sodic hydrate = 0.040 gm., and so on. In the case of univalent reagents, such as silver for estimating chlorine, the standard solution is best made of decinormal strength, that is to say, one-tenth of the atomic weight of silver = 10.8 gm. is dissolved in nitric acid, and the solution made up to 1 litre. Each c.c. of this solution will contain $\frac{1}{100000}$ of the atomic weight of silver in grammes = 0.0108 gm., and will exactly precipitate $\frac{1}{100000}$ the atomic weight of chlorine in grammes = 0.00355 gm. from any solution of a chloride in the form of argentic chloride.

In like manner, if the 1000 grain measure is used as the standard in place of the litre, 63 grains of oxalic acid would be used; but as 1000 grains is too small a quantity to make, it is better to weigh 630 grains, and make up the solution to 10,000 grain measures = 1000 dm. The solution would then have exactly the same strength as if prepared on the litre system, as it is proportionally the same in chemical power; and either solutions may be used indiscriminately for instruments graduated on both scales, bearing in mind that the substance to be tested with a c.c. burette must be weighed on the gramme system, and *vice versâ*, unless it be desired to calculate one system of weights into the other.

The great convenience of this atomic system is, that the numbers used as coefficients for calculation in any analysis are familiar, and solutions agree with each other, volume for volume. We have

hitherto, however, looked only at one side of the advantages. For technical purposes, the atomic system allows the use of all solutions of systematic strength, and simply varies the amount of substance tested according to its atomic weight.

Thus, the normal solutions say are—

Oxalic acid	= 63 gm. per litre.
Sulphuric acid	= 49 gm. „
Hydrochloric acid	= 36.5 gm. „
Nitric acid	= 63 gm. „
Sodic carbonate	= 53 gm. „
Sodic hydrate	= 40 gm. „
Ammonia	= 17 gm. „

100 c.c. of any one of these normal acids should exactly neutralise 100 c.c. of any of the normal alkalis, or the corresponding amount of pure substance which the 100 c.c. contain. In commerce we continually meet with substances used in manufactures which are not pure. It is necessary to know how much pure substance they contain.

Let us take, for instance, refined soda ash (sodic carbonate). If it were absolutely pure, 5.3 gm. of it should require exactly 100 c.c. of any normal acid to saturate it. If we therefore weigh this quantity, bring it into solution with water, add litmus, and deliver into the mixture the normal acid from a 100 c.c. burette—the number of c.c. required to saturate it will show the percentage of pure sodic carbonate in the sample. Suppose 90 c.c. are required = 90 %.

Again—a manufacturer buys common oil of vitriol, and requires to know the exact percentage of pure hydrated acid in it; 4.9 gm. is weighed, diluted with water, litmus added, and normal alkali delivered in from a 100 c.c. burette till saturated—the number of c.c. used will be the percentage of real acid. Suppose 58.5 c.c. are required = 58.5 %.

On the grain system, in the same way, 53 grains of the sample of soda ash would require 90 dm. of normal acid, also equal to 90 %.

Or, suppose the analyst desires to know the equivalent percentage of dry caustic soda, free and combined, contained in the above sample of soda ash, without calculating it from the carbonate found as above, 3.1 gm. is treated as before, and the number of c.c. required is the percentage of sodic oxide. In the same sample 52.6 c.c. would be required = 52.6 per cent. of sodic oxide, or 90 per cent. of carbonate.

The rules, therefore, for obtaining the percentage of pure substance

in any commercial article, such as alkalis, acids, and various salts, by means of systematic normal solutions such as have been described, are these—

1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ gramme atom of the substance is to be weighed for titration (according to its atomicity), and the number of c.c. required to produce the required reaction is the percentage of the substance whose atomic weight has been used.

With decinormal solutions $\frac{1}{100}$ or $\frac{1}{200}$ gramme atom is taken, and the number of c.c. required will, in like manner, give the percentage.

Where the grain system is used it will be necessary, in the case of titrating with normal solution, to weigh the whole or half the atomic weight of substance in grains, and the number of decems required will be the percentage.

With decinormal solutions $\frac{1}{10}$ or $\frac{1}{20}$ of the atomic weight in grains is taken, and the number of decems will be the percentage.

It now only remains to say, with respect to the system of weights and measures to be used, that the analyst is at liberty to choose his own plan. Both systems are susceptible of equal accuracy, and he must study his own convenience as to which he will adopt.

The normal solutions prepared on the gramme system are equally applicable for that of the grain, and *vice versa*, so that there is no necessity for having distinct solutions for each system. It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know, a weighed or measured quantity of it is brought under the acid burette and saturated exactly by aid of litmus, 32 c.c. were required. The calculation is as follows :—

The atomic weight of potassic hydrate being 56, 100 c.c. of normal acid will saturate 5.6 gm. ; therefore, as 100 c.c. are to 5.6 gm., so are 32 c.c. to x , $\frac{5.60 \times 32}{100} = 1.792$ KHO.

The simplest way, therefore, to proceed, is to multiply the number of c.c. of test solution required in any analysis, by the $\frac{1}{1000}$ or $\frac{1}{2000}$ (if bivalent) of the atomic weight of the substance sought, which gives at once the amount of substance present.

An example may be given—1 gm. of marble or limestone is taken for the estimation of pure calcic carbonate, and exactly saturated with standard nitric or hydrochloric acid—(sulphuric or oxalic acid are, of course, not admissible) 17.5 c.c. were required, therefore,

$17.5 \times .050$ (the $\frac{1}{2000}$ of the atomic weight of Ca CO_3) gives 0.875 gm., and as 1 gm. of substance only was taken = 87.5 % calcic carbonate.

In some cases it is advisable to have standard solutions based on an empirical instead of an atomic system, in which case each solution only suffices for the estimation of one special substance. This is the case in the analysis of urine and a few other substances, particulars of which will be found in their proper places.

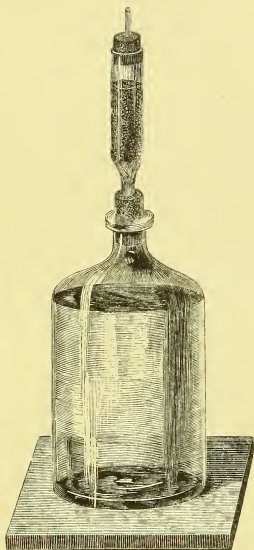


Fig. 16.

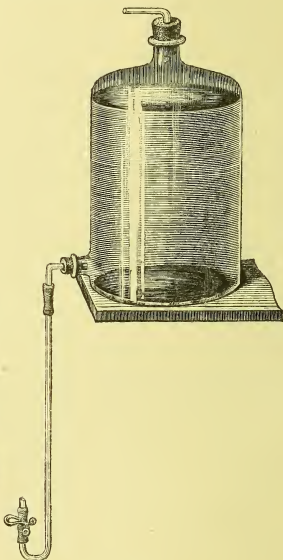


Fig. 17.

There are other test solutions which, in consequence of their proneness to decomposition, cannot be kept at any particular strength for a length of time, consequently they must be titrated on every occasion previous to being used. Stannous chloride and sulphurous acid are examples of such solutions. Special vessels have been devised for keeping solutions liable to alter in strength by access of air, as shown in figs. 16 and 17.

Fig. 16 was designed by Graham, and is especially applicable to

caustic alkaline solutions, the tube passing through the cork being filled with a mixture of Glauber's salt and quicklime, previously dried and gently ignited.

Fig. 17, designed by Mohr, is a considerable improvement upon this, since it allows of the burette being filled with the solution from the store bottle quietly, and without any access of air whatever. The vessel can be used for caustic alkalies, stannous chloride, permanganate, sulphurous acid, or any other liquid liable to undergo change by absorbing oxygen. The corks are dried and soaked in melted paraffine, and a thin layer of petroleum oil, such as is used for burning, is poured on the top of the solution, where, of course, owing to its light specific gravity, it always floats, placing an impermeable division between the air and the solution; and as this body (which should always be as pure as possible) is not affected by these reagents in their dilute state, and never need come in contact with the solution actually used, offers great advantages. Solutions not affected by contact with air should nevertheless be kept in bottles, the corks or stoppers of which are perfectly closed, and tied over with India rubber or bladder to prevent evaporation, and should further be always shaken previous to use, in case they are not quite full.

ON THE DIRECT AND INDIRECT PROCESSES OF ANALYSIS AND THEIR TERMINATION.

§ 11. THE direct method includes all those analyses where the substance under examination is decomposed by simple contact with a known quantity or equivalent proportion of some other body capable of combining with it, and where the end of the decomposition is manifested in the solution itself.

It also properly includes those analyses in which the substance reacts upon another body to the expulsion of a representative equivalent of the latter, which is then estimated as a substitute for the thing required.

Examples of the first kind are readily found in the process for the determination of iron by potassic permanganate, where the beautiful rose colour of the permanganate asserts itself as the end of the reaction.

The testing of acids and alkalies comes, also, under this class, the great sensitiveness of litmus allowing the most trifling excess of acid or alkali to alter its colour. The second is exemplified in the analysis of manganese ores, and also other peroxides and oxygen acids, by

boiling with hydrochloric acid. The chlorine evolved is estimated as the equivalent of the quantity of oxygen which has displaced it. We are indebted to Bunsen for a most accurate and valuable series of processes based on this principle.

The indirect or residual method is such that the substance to be analysed is not estimated itself, but the excess of some other body added for the purpose of combining with it or of decomposing it, and the quantity or strength of the body added being known, and the conditions under which it enters into combination being also known, by deducting the remainder or excess (which exists free) from the original quantity, it gives at once the proportional quantity of the substance sought.

An example will make the principle obvious:—Suppose that a sample of either native carbonate of lime, baryta, or strontian is to be tested. It is not possible to estimate them with standard nitric or hydrochloric acid in the exact quantity they require for decomposition. There must be an excess of acid and heat applied also to get them into solution; if, therefore, a known excessive quantity of standard acid be first added, and solution obtained, and the liquid then titrated backward with litmus and standard alkali, the quantity of free acid can be exactly determined, and consequently that which is combined also.

In some analyses it is necessary to add a substance which shall be an indicator of the end of the process; such, for instance, is litmus in alkalimetry, potassic chromate in silver and chlorine, and starch in iodine, estimations.

There are other processes, the end of which can only be determined by an indicator separate from the solution; such is the case in the estimation of iron by potassic bichromate, where a drop of the liquid is brought into contact with another drop of solution of red potassic prussiate on a white slab or plate, when a blue colour ceases to form by contact of the two liquids, the end of the process is reached.

The latter is somewhat less reliable, in point of delicacy, than the others, but nevertheless, with care and practice, is susceptible in most cases of very tolerable accuracy.

PART II.

ANALYSIS BY SATURATION.

ALKALIMETRY AND ACIDIMETRY.

§ 12. GAY LUSSAC based his system of alkalimetry upon a titrated solution of sodic carbonate, with a corresponding solution of sulphuric acid, and as this was devised mainly for the use of soda manufacturers it was doubtless the best system for that purpose. It possesses the recommendation that a pure standard solution of sodic carbonate can be more readily obtained than any other form of alkali. Mohr has introduced the use of caustic alkali instead of a carbonate, the strength of which is established by a standard solution of oxalic or sulphuric acid. The principal advantage in the latter system is, that in testing the strength of acids with a caustic alkali, the well-known interference produced by carbonic acid is avoided. The caustic solutions of soda, potash, or ammonia should be kept in bottles like those shown in figs. 16 and 17, so as to prevent their absorbing carbonic acid.

INDICATORS USED IN ALKALIMETRY.**1. Litmus Solution.**

§ 13. IN testing both acids and alkalies it is necessary to employ a solution of litmus as indicator, which is best prepared by taking about 10 grammes of the solid material, and digesting it with half a litre of distilled water for a few hours in a warm place, decanting the clear liquid from the sediment, adding a few drops of dilute nitric acid so as to produce a violet colour, and preserving it in an open bottle with narrow neck and bulb tube for removing drops as may be required—fig. 18.

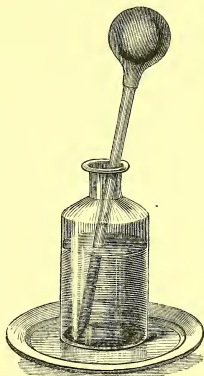


Fig. 18.

If at any time the colour of the liquid should partially disappear, it may be restored again by exposing it to the air in an open dish.

Litmus, prepared and kept in this way, is very sensitive to dilute acids and alkalies; with the slightest excess of oxalic, sulphuric, hydrochloric, or nitric acids it gives a pink red, and with caustic soda or potash, a blue colour; with ammonia or the bicarbonated alkalies it retains its violet colour, and the same with most of the neutral salts of the weak acids, such as sodic or ammonic acetate or borax.

Free carbonic acid interferes considerably with the production of the blue colour, and its interference in titrating acid solutions with alkaline carbonates can only be got rid of by boiling the liquid during the operation, in order to displace the gas from the solution. If this is not done, it is easy to overstep the exact point of neutrality in endeavouring to produce the blue colour; the same difficulty is also found in obtaining the pink red when acids are used for titrating alkaline carbonates, hence the great value of the caustic alkaline solutions free from carbonic acid in acidimetry.

Litmus paper is simply made by dipping strips of filtering paper in the solution and drying them; if required red, the liquid is slightly acidified.

2. Cochineal Solution.

This indicator possesses the advantage over litmus that it is not so much modified in colour by the presence of carbonic acid. It can also be used with the best effect with solutions of the alkaline earths, such as lime and baryta water; the colour with pure alkalies and earths is especially sharp and brilliant. The solution is made by digesting about 3 gm. of powdered cochineal in a quarter litre of a mixture of 4 parts water and 1 part alcohol. Its natural colour is yellowish red, and is turned to violet by alkalies; mineral acids restore the original colour; it is not so easily affected by weak organic acids as litmus, and therefore for these acids the latter is preferable.

3. Turmeric Paper.

Pettenkofer, in his estimation of carbonic acid by baryta water, prefers turmeric paper as an indicator. The paper is prepared by digesting pieces of the root in weak alcohol, and dipping strips of stout filter paper therein, drying and preserving them in the dark. The excess of baryta is estimated by $\frac{N}{10}$ nitric or oxalic acid, and the ending of the process is indicated when a drop of the mixture brought in contact with the paper produces no brown tinge at the outer edge of the circle.

It is said that a solution of rosolic acid (prepared from pure

phenol) is a better indicator than turmeric paper; the solution is used precisely as litmus.

PREPARATION OF THE NORMAL ACID AND ALKALINE SOLUTIONS.

1. Normal Sodid Carbonate

= 53 gm. Na^2CO^3 per litre.

§ 14. THIS solution is made by dissolving 53 gm. of pure and dry sodid monocarbonate in distilled water, and diluting to 1 litre at 16° . If the salt is not at hand, the solution may be made as follows:—

About 85 gm. of pure sodid bicarbonate is heated to dull redness, not to fusion, in a platinum, silver, or porcelain crucible, for fully ten minutes, to expel the carbonic acid, then placed under an exsiccator to cool; when placed upon the balance it will be found that very little more than 53 gm. remain. The excess is removed as quickly as possible, and the contents of the crucible emptied into a beaker, then wash out the crucible into the beaker, and as soon as the salt is dissolved, decant the solution into a litre flask, rinse repeatedly, and make up the litre exactly with distilled water, at 16° .

2. Normal Sulphuric Acid

= 49 gm. H^2SO^4 per litre.

About 30 c.c. of pure sulphuric acid of sp. gr. 1·840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to the litre. It must now be tested by the normal alkali, which is best done by putting 10 c.c. of the latter into a small beaker or flask with litmus, and from a 10 or 12 c.c. pipette, divided into $\frac{1}{10}$ c.c., allowing the acid to flow until the point of neutrality is reached. If more than 10 c.c. are required the acid is too weak; if less, too strong. If the acid from which the solution was made was of the sp. gr. mentioned, it will generally be too strong, which is preferable. Suppose, therefore, it required 8·9 c.c. to saturate the 10 c.c. of alkali, 890 c.c. will be required to make one litre of standard acid; remove, therefore, the excess from the cylinder and dilute to exactly one litre. Now, test again with the pipette, if the previous examination was correct, 10 c.c. of each solution should exactly neutralise each other.

The solution may also be controlled by precipitation with baric chloride, in which case 10 c.c. should produce as much baric sulphate as is equal to 0·49 gm. of sulphuric acid, or 49 gm. per litre.

3. Normal Oxalic Acid

= 63 gm. $C^2O^4H^2$, $2H^2O$ per litre.

This solution possesses the advantage that it may be established direct, by weighing 63 gm. or $\frac{1}{2}$ gramme atom of the pure crystallised acid in a litre of water.

The acid should be recrystallised repeatedly, thoroughly air dried, but not in the slightest effloresced. The solution is apt to deposit some of the acid at low temperatures, but otherwise keeps well, and will bear heating without volatilising the acid.

4. Normal Hydrochloric Acid

= 36.5 gm. HCl per litre.

It has been shown by Roscoe and Dittmar (Chem. Soc. Q. J. vol. 12) that a solution of hydrochloric acid containing 20.2 per cent. of the gas when boiled at about 760 m.m. pressure, loses acid and water in the same proportion, and the residue will therefore have the constant composition of 20.2 % = specific gravity of 1.10. About 181 gm. of liquid acid of this gravity, diluted to 1 litre, serves very well to form an approximate normal acid.

The actual strength may be determined by $\frac{N}{10}$ silver solution, or by titration with an exactly weighed quantity of pure sodic monocarbonate. Hydrochloric acid is useful on account of its forming soluble compounds with the alkaline earths, but it has the disadvantage of volatilising at boiling heat. Dittmar says that this may be prevented by adding a few grammes of sodic sulphate; in many cases this would be inadmissible, for the same reason that sulphuric acid cannot be used. Standard hydrochloric acid is chiefly valuable as a check to alkaline solutions, inasmuch as, owing to the great delicacy of the reaction between chlorine and silver, the strength of a solution of the acid may be exactly found, and thus serves more especially as a standard for the caustic alkaline solutions.

5. Normal Nitric Acid

= 63 gm. HN^5O per litre.

In order to obtain a rigidly exact normal acid, it is advisable to graduate it by pure calcic carbonate, either in the form of the purest Iceland spar, as recommended by Pincus, or by artificial carbonate, prepared with great care by precipitating pure calcic chloride with am-

monic carbonate, and boiling the resulting precipitate until it becomes dense; it is then to be washed thoroughly with hot water, dried, ignited gently, and preserved in bottles closed with a chloride of calcium tube.

By means of either of these forms of calcic carbonate, it is possible at any time to titrate a dilute nitric acid, so as to bring it to the normal state, but as more acid must be used for the decomposition than is actually required to saturate the lime and expel the carbonic acid, the excess must be estimated by the help of normal alkali.

It is a question whether the complication introduced by this method is more exact in its results than by titrating the nitric acid direct by means of sodic carbonate. If the very purest sodic carbonate is used, and every precaution taken in igniting and weighing it, there cannot be much scope for error; nevertheless, it is desirable to check the results in every possible way, and as pure calcic carbonate is not difficult to obtain, and does not contract moisture like sodic carbonate, it is a reliable basis upon which to work.

The nitric acid used should be colourless, free from chlorine and nitrous acid, sp. gr. from 1.35 to 1.4. If coloured from the presence of nitrous or hyponitrous acids, it should be mixed with two volumes of water, and boiled until white. When cold it may be diluted and titrated as above. 1 gm. of pure Iceland spar in small pieces should require 20 c.c. of acid, supposing it to be rigidly normal; if slightly stronger or weaker, the exact difference must be found, so that a constant factor may be obtained by which to bring it by calculation to the normal state.

Lime, baryta, and strontia, in the caustic state, or combined with carbonic acid, are dissolved by the aid of heat in an excess of normal acid, and then titrated with normal alkali. Chlorides and nitrates of the same bases are precipitated hot with ammoniac carbonate containing caustic ammonia, thoroughly washed with hot water on a filter, and both filter and precipitate, while still moist, pushed through the funnel into a flask, and titrated as above; by deducting the number of c.c. of alkali from the original quantity of acid used, the proportion of pure base, or its compounds, may be obtained.

6. Normal Caustic Alkali

= 40 gm. NaHO, 56 gm. KHO, or 17 gm. NH^3 per litre.

May consist of either soda, potash, or (less recommendably) ammonia. The two first are prepared from pure carbonates by the aid of fresh-burnt lime as follows:—

Two parts of pure sodic or potassic carbonate are to be dissolved in 20 parts of distilled water and boiled in a clean iron pot; during the boiling one part of fresh quick-lime, made into a cream with water, is to be added little by little, and the whole boiled until all the carbonic acid is removed, which may be known by the clear solution producing no effervescence on the addition of dilute acid; cover the vessel closely, and set aside to cool and settle; when cold, the clear supernatant liquid is to be poured or drawn off and titrated by normal acid, and made of the proper strength as directed for sulphuric acid.

The trouble of making the soda solution by aid of lime may be avoided with advantage by using the pure sodic hydrate manufactured from metallic sodium. It may be obtained perfectly pure and free from carbonic acid. About 42 gm. is dissolved in 800 c.c. of water, titrated with normal acid, and diluted so that it corresponds with the acid, volume for volume.

Normal caustic ammonia is simply made by diluting the strong and freshly made commercial solution, so that volume for volume it corresponds with normal acid.

In preparing any of these three alkaline solutions, they should be exposed as little as possible to the air, and when the strength is finally settled, should be preserved in one of the bottles shown in fig. 16 or 17.

ESTIMATION OF THE CORRECT STRENGTH OF STANDARD SOLUTIONS NOT STRICTLY NORMAL OR SYSTEMATIC.

§ 15. In discussing the preparation of the foregoing standard solutions, it has been assumed that they shall be strictly and absolutely correct,—that is to say, if the same litre measure be filled first with any alkaline solution, then with an acid solution, and the two mixed together, a perfectly neutral solution shall result, so that a drop or two either way will upset the balance.

Where it is possible to weigh directly a pure dry substance, this approximation may be very closely reached. Sodic monocarbonate, for instance, admits of being thus accurately weighed, and so also does oxalic acid. On the other hand, the caustic alkalies cannot be so weighed, nor can the liquid acids. An approximate quantity, therefore, of these substances must be taken, and the exact power of the solution found by experiment.

In titrating such solutions it is exceedingly difficult to make them so exact in strength that the precise quantity, to a drop or two, shall neutralise each other. In technical matters a near approximation may be sufficient, but in scientific investigations it is of the greatest importance that the utmost accuracy should be obtained ; it is, therefore, advisable to ascertain the actual difference, and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a standard sulphuric acid is prepared which does not rigidly agree with the normal sodic carbonate, not at all an uncommon occurrence, as it is exceedingly difficult to hit the precise point ; but in order to find out the exact difference, about 3 gm. of absolutely pure sodic bicarbonate is to be ignited in a platinum crucible until converted into monocarbonate, then placed under the exsiccator and allowed to cool ; when placed on the balance, suppose the weight found to be 1.9 gm., it is then dissolved and titrated with the standard acid, of which 36.1 c.c. were required to reach the exact neutral point.

If the acid were rigidly exact it should require 35.85 c.c. ; in order, therefore, to find the factor necessary to bring the quantity of acid used in the analysis to the normal strength, the number of c.c. actually used must be taken as the divisor for the number which should have been used had the acid been strictly normal, consequently—

$$\frac{35.85}{36.1} = 0.993 ;$$

the quotient 0.993 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid used in any analysis in order to reduce it to normal strength, and should be marked upon the bottle in which it is kept.

On the other hand, suppose that the acid is too strong, and that 35.2 c.c. were required instead of 35.85,

$$\frac{35.85}{35.2} = 1.0184 ;$$

1.0184 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid in order to bring it to the normal strength.

It is, of course, taken for granted that the original normal solu-

tion, from which the others are graduated, shall be rigidly exact, otherwise considerable errors will inevitably occur at every step.

Under all circumstances, it is safer to prove the strength of any standard solution by experiment, even though its constituent has been accurately weighed in the dry and pure state.

Further, let us suppose that a solution of caustic soda is to be made by means of lime, as described previously—after pouring off the clear liquid, water is added to the sediment to extract more alkaline solution ; by this means we may obtain two solutions, one of which is stronger than necessary, and the other weaker. Instead of mixing them in various proportions and repeatedly trying the strength, we may find, by one experiment and calculation, the proportions of each necessary to give a normal solution, thus :—

The exact actual strength of each solution is first found by separately running into 10 c.c. of normal acid as much of each alkaline solution as will exactly neutralise it. We have, then, in the case of the stronger solution, a number of c.c. required less than 10. Let us call this number V .

In the weaker solution the number of c.c. is greater than 10, represented by v . A volume of the stronger solution = x will saturate 10 c.c. of normal acid as often as V is contained in x .

A volume of the weaker solution = y will, in like manner, saturate $\frac{10y}{v}$ c.c. of normal acid ; both together saturate $\frac{10x}{V} + \frac{10y}{v}$, and the volume of the saturated acid is precisely that of the two liquids, thus—

$$\frac{10x}{V} + \frac{10y}{v} = x + y.$$

Whence

$$10. vx + 10. Vy = Vvx + Vvy$$

$$vx(10 - V) = Vy(v - 10).$$

And lastly,

$$\frac{x}{y} = \frac{V(x - 10)}{v(10 - V)}.$$

An example will render this clear. A solution of caustic soda was taken, of which 5.8 c.c. were required to saturate 10 c.c. normal acid ; of another solution, 12.7 c.c. were required. The volumes of each necessary to form a normal solution were found as follows :—

$$\begin{aligned} 5.8(12.7 - 10) &= 15.66 \\ 12.7(10 - 5.8) &= 53.34. \end{aligned}$$

Therefore, if the solutions are mixed in the proportion of 15.66 c.c. of the stronger with 53.34 c.c. of the weaker, a correct solution ought to result. This same principle of adjustment is, of course, applicable to standard solutions of every class.

Again, suppose that a standard solution of sulphuric acid has been made approximating as nearly as possible to the normal strength, and its exact value found by precipitation with baric chloride, or a standard hydrochloric acid with argentic nitrate, and such a solution has been calculated to require the coefficient 0.995 to convert it to normal strength,—by the help of this solution, though not strictly normal, we may titrate an approximately normal alkaline solution thus. Two trials of the acid and alkaline solutions show that 50 c.c. alkali = 48.5 c.c. acid, having a coefficient of $0.995 = 48.25$ c.c. normal; then, according to the equation, $x \cdot 50 = 48.26$ is the required coefficient for the alkali.

$$= \frac{48.25}{50} = 0.965.$$

And here, in the case of the alkaline solution being sodic carbonate, we can bring it to exact normal strength by a calculation based on the atomic weight of the salt, thus—

$$1 : 0.965 = 53 : 51.145.$$

The difference between the two latter numbers is 1.855 gm., and this weight of pure sodic carbonate, added to 1 litre of the solution, will bring it to normal strength.

METHOD OF PROCEDURE IN TITRATING ALKALIES AND ACIDS.

Salts of Soda and Potash.

§ 16. THE necessary quantity of substance being weighed or measured, as the case may be, and mixed with distilled water to a proper state of dilution, a sufficient quantity of litmus to produce a distinct blue or red colour is added, and the solution is ready for the burette. Let us suppose that sodic carbonate is to be titrated, the acid from the burette is allowed to flow in until a claret tinge begins to appear. This takes place some time before the complete quantity of acid is added, owing to the liberation of carbonic acid. In order to dissipate the carbonic acid, the liquid must be heated to

boiling over a spirit or gas lamp, when the blue colour will again appear. Continue to add the acid a few drops at a time, and repeat the heating until all the carbonic acid is expelled and a distinct pink red colour is produced in the liquid by the final drop of acid. It is always advisable to make a second and conclusive test of the alkali, and, therefore, the first supplies a guide to the quantity of acid required, and allows a more exact method of procedure towards the end of the process.

In the examination of samples of ordinary soda or pearlash, it is advisable to proceed as follows :—

Powder and mix the sample thoroughly, weigh 10 gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture; wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 c.c. with distilled water in a $\frac{1}{2}$ litre flask, after mixing it thoroughly take out 50 c.c. = 1 gm. of alkali with a pipette, and empty it into a small flask, bring the flask under a burette containing normal acid and graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., allow the acid to flow cautiously as before directed, until the neutral point is reached, the process may then be repeated several times if necessary, in order to be certain of the correctness of the analysis.

As the presence of carbonic acid always tends to confuse the exact end of the process, the difficulty may be overcome by allowing more acid than is needed to flow into the alkali, boiling to expel the carbonic acid, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes to violet blue; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of test acid necessary to saturate the 1 gm. of alkali is ascertained.

This residual or backward method of testing gives a very sharp and sure result, as there is no carbonic acid present to interfere with the colour of the liquid. An example will make the plan clear :—

50 c.c. of the solution of alkali prepared as directed, and which is equal to 1 gm. of the original sample, is put into a flask and exactly 20 c.c. of normal acid allowed to flow into it, it is then boiled and shaken till all carbonic acid is expelled, and normal caustic alkali added backward till the neutral point occurs; the quantity required was 3.4 c.c., which deducted from 20 c.c. of acid, leaves 16.6 c.c. The following calculation, therefore, gives the percentage of real

alkali, supposing it to be soda—31 is the atomic weight of dry soda, NaO ,* and 1 c.c. of the acid is equal to 0.031 gm., therefore, 16.6 c.c. is multiplied by 0.031, which gives 0.5146, and as 1 gm. was taken, the decimal point is moved two places to the right, which gives 51.46 per cent. of real alkali; if calculated as carbonate, the 16.6 would be multiplied by 0.053 (53 being the $\frac{1}{2}$ atomic weight of Na_2CO_3), which gives 0.8798 gm. = 87.98 per cent.

The alkaline salts of commerce, and also alkaline lyes used in soap, paper, starch, and other manufactories, consist generally of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportion in which these mixtures occur, the total alkaline power of a weighed or measured quantity of substance is ascertained by normal acid and noted, a like quantity is then brought into solution to about 150 c.c., in a 300 c.c. flask, heated to boiling, and enough solution of baric chloride added to remove all the carbonic acid from the soda or potash, there must be an excess of chloride, but as it does not interfere with the accuracy of the result the exact quantity is of no consequence.

The flask is now filled up to the 300 c.c. mark with distilled water, corked, and put aside to settle. When the supernatant liquid is clear, take out 100 c.c. with a pipette, and titrate with normal nitric acid to the neutral point. The number of c.c. multiplied by 3, will be the quantity of acid required for the caustic alkali in the original weight of substance, because only $\frac{1}{3}$ was taken for analysis.

The precipitated baric carbonate may be thrown upon a filter, washed well with hot water, and titrated with normal nitric acid, as described further on, if the operator chooses, instead of the original analysis for the total alkalinity, or both plans may be adopted as a check upon each other.

The principle of this method is, that when baric chloride is added to a mixture of caustic and carbonated alkali, the carbonic acid of the latter is precipitated as an equivalent of baric carbonate, while the equivalent proportion of caustic alkali remains in solution as baric hydrate. By multiplying the number of c.c. of acid required to saturate this free alkali with the atomic weight of either caustic potash or soda, according to circumstances, the quantity of substance originally present in this state will be obtained.

As caustic baryta absorbs carbonic acid very readily when exposed

* The commercial standard often used is 32.

to the atmosphere, it is preferable to allow the precipitate of carbonate of baryta to settle in the flask as here described, rather than to filter the solution as recommended by some operators.

AMMONIA



§ 17. IN estimating the strength of solutions of ammonia by the alkalimetric method, it is better to avoid the tedious process of weighing any exact quantity, and to substitute for it the following plan, which is applicable to most liquids for the purpose of ascertaining both their absolute and specific weights.

Let a small and accurately tared flask, beaker, or other convenient vessel be placed upon the balance, and into it 10 c.c. of the ammoniacal solution delivered from a very accurately graduated 10 c.c. pipette. The weight found is, of course, the absolute weight of the liquid in grammes; suppose it to be 9.65 gm., move the decimal point one place to the left, and the specific weight or gravity is at once given (water being 1), which in this case is 0.965.

The 10 c.c., weighing 9.65 gm., was now titrated with normal acid, of which 49 c.c. were required, therefore $49 \times 0.017 = 0.833$ gm. $\text{NH}^3 = 8.64$ per cent. of real ammonia; according to Otto's table 9.65 sp. gr., is equal to 8.50 per cent. Ammonic carbonate, and a mixture of the same with bicarbonate, as it most commonly occurs in commerce, may be titrated direct with normal acid for the percentage of real ammonia. The carbonic acid can be determined by precipitation hot with baric chloride, and when the precipitate is well washed, dissolving it with an excess of normal acid and titrating backward with normal alkali, as described more fully under the head of alkaline earths, the number of c.c. of acid used multiplied by 0.022 (the $\frac{1}{2}$ at. wt. of CO^2) will give the weight of carbonic acid present in the sample.

Instead of the 10 c.c., a 10 dm. pipette can be used for taking specific gravity, in which case the decimal point is moved two places to the left, grain weights being of course used in the weighing.

It must be borne in mind that this system can only be used properly with tolerably delicate balances and very accurate pipettes. The latter should invariably be tested by taking the sp. gr. of distilled water at 16°C. , according to the plan described.

The ammonia contained in rain or other waters can be estimated

according to Boussingault's researches, by distilling off about one-third of the water under examination, with the addition of a little caustic potash or quicklime, the exact measures both of the distillate and the original water being known, the former may be titrated with normal acid, and the quantity of ammonia in the original specimen at once ascertained by a slight calculation ; generally speaking, not less than a couple of litres should be used for the examination.

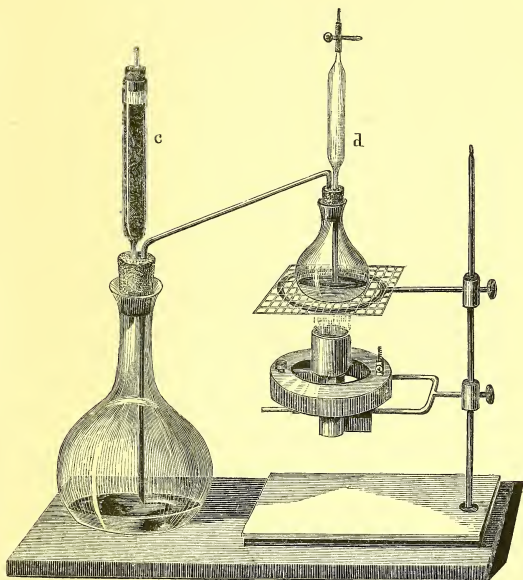


Fig. 19.

AMMONIA IN COMBINATION ESTIMATED BY DISPLACEMENT WITH FIXED ALKALIES.

THE apparatus shown in fig. 19 is of great value in determining accurately all the forms of ammonia which can be displaced by soda, potash, or lime, and the gas so evolved collected in a known volume

in excess of normal acid, the excess of acid being afterwards found by residual titration with normal alkali.

The little flask, holding about 200 c.c. and placed upon the wire gauze, contains the ammoniacal substance. The tube *d* is filled with strong solution of caustic potash or soda; the large flask holds about a pint, and contains a measured quantity of normal acid, part being contained in the tube *c*, which is filled with broken glass, and through which the normal acid has been poured.

The substance to be examined is weighed and put into the distilling flask with a little water, the apparatus then being made tight at every part, some of the caustic alkali is allowed to flow in by opening the clip, and the spirit lamp is lighted under it.

The contents are brought to gentle boiling, taking care that the froth, if any, does not enter the distilling tube. It is well to use a common spirit lamp held under the flask in the hand; in case there is any tendency to boil over, the lamp can be removed immediately and the flask blown upon by the breath, which brings down the temperature in a moment. In examining guano and other substances containing ammoniacal salts and organic matter by this means, the tendency to frothing is considerable, and unless the above precautions are taken, the accuracy of the results will be interfered with.

The distilling tube has both ends cut slantwise, and the lower end just reaches to the surface of the acid, to which a little litmus is added. The quantity of acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with normal alkali.

It is advisable to continue the boiling for say ten or fifteen minutes, then rest for the same time to allow all the ammonia to be absorbed. Lastly, boil once or twice for a minute or so, take away the lamp, and allow the apparatus to stand a few minutes to cool; then opening the clip, blow through the pipette so as to force all the remaining gas into the acid vessel. The tube *c* must be washed out into the flask with distilled water, so as to carry down the acid with any combined gas which may have reached it. The titration then proceeds as usual. This process is particularly serviceable for testing commercial ammoniacal salts, gas liquor, &c.; the results are very satisfactory.

Instead of the foregoing direct plan, in the case of tolerably pure neutral ammoniacal salts, a simpler indirect one can be used, which is as follows:—

If the ammoniacal salt be boiled in an open flask with solution

of sodic or potassic carbonate, or caustic alkali, the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the strength and quantity of the alkaline solution are known, the excess beyond that, necessary to supplant the ammonia, can be found by the ordinary system of titration. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

Example, 1.5 gm. of purest sublimed ammoniac chloride was brought into a flask with 40 c.c. of normal sodic carbonate, and boiled till all ammonia was expelled, then titrated backward with normal sulphuric acid, of which 11.9 c.c. were required; this left 28.1 c.c. of normal alkali, which multiplied by 0.05346 gave 1.502 gm., instead of 1.5 gm. originally taken.

CONVERSION OF NITROGEN IN NITROGENOUS SUBSTANCES INTO AMMONIA, AND ESTIMATION BY PELIGOT'S PROCESS.

§ 18. THIS process consists in heating a convenient quantity of the dried substance in a combustion tube with soda lime, by which the nitrogen is converted into ammonia, and this latter being led into a measured volume of normal sulphuric, hydrochloric, or nitric acid contained in Will and Varrentrapp's bulb apparatus, combines with its equivalent quantity; the solution is then titrated residually with standard alkali for the excess of acid, and thus the quantity of ammonia found.

As the combustion tube with its arrangements for organic analysis is well known, and described in any of the standard books on general analysis, it is not necessary to give a description here.

Instead of leading the ammonia through normal acid, hydrochloric acid of unknown strength may be used, the liquid brought into the distilling apparatus, and the ammoniac chloride estimated by the process described above.

When it is necessary to estimate very minute portions of ammonia, it may be brought into the form of chloride, and estimated by decinormal silver solution, as described, in § 36, or in many cases preferably by Nessler's test, described in the section on Water analysis,

‡ 19. TABLE FOR THE SYSTEMATIC ANALYSIS OF
ALKALIES, ALKALINE EARTHS, AND ACIDS.

Substance.	Formula.	Atomic Weight.	Quantity to be weighed so that 1 c.c. Normal Solution = 1 per cent. of substance.	Normal Factor.*
Soda	Na_2O	62	3.1 gm.	0.031
Sodic Hydrate . .	NaHO	40	4.0 gm.	0.040
Sodic Carbonate . .	Na_2CO_3	106	5.3 gm.	0.053
Sodic Bicarbonate .	NaHCO_3	84	8.4 gm.	0.084
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Potash	K_2O	94	4.7 gm.	0.047
Potassic Hydrate . .	KHO	56	5.6 gm.	0.056
Potassic Carbonate .	K_2CO_3	138	6.9 gm.	0.069
Potassic Bicarbonate	KHCO_3	100	10.0 gm.	0.100
<hr/>				
Ammonia	NH_3	17	1.7 gm.	0.017
Ammonic Carbonate	$(\text{NH}_4)_2\text{CO}_3$	96	4.8 gm.	0.048
<hr/>				
Lime (Calcic Oxide) .	CaO	56	2.8 gm.	0.028
Calcic Hydrate . .	CaH_2O_2	74	3.7 gm.	0.037
Calcic Carbonate . .	CaCO_3	100	5.0 gm.	0.050
<hr/>				
Barytic Hydrate . .	BaH_2O_2	171	8.55 gm.	0.0855
Do. (Crystals) . .	$\text{BaO}^2\text{H}^2(\text{H}_2\text{O})^8$	315	15.75 gm.	0.1575
Barytic Carbonate .	BaCO_3	191	9.85 gm.	0.0985
<hr/>				
Strontia	SrO	103.5	5.175 gm.	0.0575
Strontic Carbonate .	SrCO_3	147.5	7.375 gm.	0.07375
<hr/>				
Magnesia	MgO	40	4.00 gm.	0.040
Magnesian Carbonate .	MgCO_3	84	4.80 gm.	0.048
<hr/>				
Nitric Acid	HNO_3	63	6.3 gm.	0.063
Hydrochloric Acid .	HCl	36.5	3.65 gm.	0.0365
Sulphuric Acid . .	H_2SO_4	98	4.9 gm.	0.049
Oxalic Acid	$\text{C}^2\text{O}^4\text{H}^2$	126	6.3 gm.	0.063
Acetic Acid	$\text{C}^2\text{O}^2\text{H}^4$	60	6.0 gm.	0.060
Tartaric Acid . . .	$\text{C}^4\text{O}^6\text{H}^6$	150	7.5 gm.	0.075
Citric Acid	$\text{C}^6\text{O}^7\text{H}^8 + \text{H}_2\text{O}$	210	7.0 gm.	0.070

* This is the coefficient by which the number of c.c. of normal solution used in any analysis is to be multiplied in order to obtain the amount of pure substance present in the material examined.

If grain weights are used instead of grammes, the decimal point must be moved one place to the right to give the necessary weight for examination; thus sodic carbonate, instead of 5.3 gm., would be 53 grains—the normal factor in this case would also be altered to 0.53.

ALKALINE EARTHS.

§ 20. NORMAL, nitric, or hydrochloric acids are the best agents for the titration of the caustic and carbonated alkaline earths, inasmuch as the resulting compounds are all soluble. Nitric acid is preferable on account of its non-volatile character when heated, and as all the insoluble forms of these bodies must be estimated by the residual method, that is to say, dissolved first in an excess of normal acid heated to dispel carbonic acid in the case of carbonates, and the amount of excess found by normal alkali, the tendency of hydrochloric acid to dissipate by heating is a drawback. This cannot, moreover, be remedied by the use of sodic sulphate, as in most cases insoluble sulphates would be produced and interfere with the accuracy of the operation, but the amount of loss by heating very dilute solutions of HCl may be practically disregarded.

The amount of calcic or calcic and magnesian carbonates dissolved in ordinary waters may be very readily, and with tolerable accuracy, found by taking 200 or 300 c.c. of the water, adding about 1 c.c. of cochineal tincture, and titrating cautiously with $\frac{N}{10}$ nitric acid until the original violet colour gives place to yellow red.

A check trial was made by digesting pure calcic carbonate in water charged with carbonic acid gas,—by titration 1.05 gm. per litre was found, by evaporation 1.09 gm.; with mixtures of calcic and magnesian carbonates, there will, of course, be no distinction between the two,—the whole will be expressed as calcic carbonate, in the same way as by Clark's soap test.

TITRATION OF ACIDS.

§ 21. THIS operation is simply the reverse of all that has been said of alkalies, and depends upon the same principles as have been explained in alkalimetry.

With free liquid acids such as hydrochloric, sulphuric, or nitric, the strength is generally taken by means of the hydrometer or specific gravity bottle, and the amount of real acid in the sample ascertained by reference to the tables constructed by Otto, Bineau, or Ure. The specific gravity may very easily be taken with the pipette as recommended with ammonia, and of course the real acid may be quickly estimated by normal caustic alkali.

1. Hydrochloric Acid.

Example: 5 c.c. of white and tolerably pure hydrochloric acid was put into a small tared bottle, and the weight found to be 5.6 gm.; this divided by 5, gave the sp. gr. as 1.12. It was diluted and titrated with normal alkali, of which 37.1 c.c. were required; this multiplied by 0.0365, gave 1.354 gm. = 24.2 %. Ure's table gives 24.46 for the same sp. gr.

In order to ascertain the percentage of hydrochloric acid gas in any sample, it is only necessary to multiply the weight of gas found by normal alkali by 100, and divide by the weight of acid originally taken for analysis; the quotient will be the percentage. Or, simpler than this, if the $\frac{1}{100}$ atom in grammes, 3.646 gm., or 1 atom in grains, = 36.46 grs., be weighed, the number of c.c. or decems will be the percentage respectively.

2. Nitric Acid.

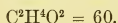
Example: 5 c.c. of pure nitric acid weighed 6.07 gm., the sp. gr. was therefore 1.215; the quantity of normal alkali required was 33 c.c., which multiplied by 0.054, gave 1.782 gm. $\text{NO}^5 = 29.3\%$. Ure's table gives 29.5% for the same specific gravity.

3. Sulphuric Acid.

Example: 10 c.c. of concentrated white sulphuric acid was weighed, and found to be 18.25 gm.; sp. gr., therefore, 1.825.

In consequence of the great concentration and high sp. gr. of this acid, it is best to use only 1 or 2 c.c. for analysis; after the specific gravity is taken, 1 c.c. may be titrated, taking care that a very fine and accurate pipette is used for the purpose, or if this is not at hand, it must be weighed direct upon the balance.

2 gm. of the above acid was titrated, and found to require 37 c.c. of normal alkali = 90.65% hydrated acid, which agrees exactly with Bineau's table.

4. Acetic Acid.

In consequence of the anomaly existing between the specific gravity of acetic acid and its strength, the hydrometer gives no

uniformly reliable indication of the latter, and consequently the volumetric method is peculiarly suitable for ascertaining the value of acetic acid in all its forms. For most technical purposes normal caustic alkali may be used as the saturating agent; but a slight error occurs in this method, from the fact that neutral acetates have an alkaline reaction on litmus; the error, however, is very small, if care be taken to add the alkali till a distinct blue colour is reached. As acetic acid is volatile at high temperatures, normal carbonate of soda must not be used for titrating it, as it would necessitate heat to expel the carbonic acid.

Example: 5 c.c. of Beaufoy's acetic acid weighed 5.206 gm. = 1.041 sp. gr. The quantity of normal alkali required to saturate it was 27.1 c.c., which multiplied by 0.60 = 1.626 gm. acetic acid, or 32.5%. For the ordinary vinegars, there is no necessity to take the specific gravity into the question. 5 or 10 c.c. may be taken as 5 or 10 gm. Malt or coloured vinegar must be copiously diluted, in order that the change in the colour of the litmus may be distinguished; where the colour is such as to make the end of the process doubtful, recourse must be had to litmus paper, upon which little streaks should be made from time to time with a fine glass rod or a small feather.

Several processes have at various times been suggested for the accurate and ready estimation of acetic acid, among which I may mention that of C. Greville Williams, by means of a standard solution of lime syrup; the results he obtained seemed very satisfactory; but where absolute accuracy is required in every possible form and colour of acetic acid, C. Mohr's process is undoubtedly the most reliable.

It consists in adding to a known quantity of the acid an excess of carbonate of baryta or lime in fine powder; the pure calcic carbonate described in the chapter on alkaline earths is preferable, as it dissolves more readily than the baryta. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the carbonic acid, and to complete the saturation; the residual carbonate is then brought upon a filter, washed with boiling water, and titrated with normal acid and alkali.

This process is applicable in all cases, and however dark the colour may be; in testing the impure brown pyroligneous acid it is especially serviceable. Pettenkofer titrates acetic acid or vinegar with excess of baryta water, and estimates the excess of the latter with $\frac{N}{10}$ nitric or oxalic acid by the help of turmeric paper.

The titration of acetic acid or vinegar may also be performed by Kieffer's ammonio-cupric solution described below.

KIEFFER'S NORMAL AMMONIO-CUPRIC SOLUTION FOR ACIDIMETRY FOR TECHNICAL PURPOSES.

§ 22. THIS acidimetric solution is prepared by dissolving pure cupric sulphate in warm water, and adding to the clear solution liquid ammonia, until the bluish green precipitate which first appears is nearly dissolved ; then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in $\frac{1}{6}$ or $\frac{1}{16}$ c.c. into 10 or 20 c.c. of normal sulphuric or nitric acid (not oxalic) ; while the acid remains in excess, the bluish green precipitate which occurs as the drop falls into the acid rapidly disappears ; but so soon as the exact point of saturation occurs, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid.

The process is especially serviceable for the estimation of the free acid existing in certain metallic solutions, *i.e.*, mother liquors, &c., where the neutral compounds of such metals have an acid reaction on litmus,—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel ; it is also applicable to acetic and the mineral acids.

The value of the process in any given case depends upon the insolubility of the cupric oxide in the neutral solution which results from the combination of the ammonia and acid. Carey Lea (*vide* "Chemical News," Oct. 12th, 1861, p. 196) has objected to this process on the ground that the precipitate (which he supposes to be a basic sulphate of copper) is not totally insoluble in certain neutral solutions when concentrated, such as ammoniac sulphate, nitrate, or chloride, and he thinks it strange that so experienced a chemist as Mohr should be led into the error of highly recommending such an acidimetric process, alleging that a different result would be obtained between testing a solution containing 5 gm. of sulphuric acid with 5 gm. of ammoniac sulphate, and the same quantity of acid with 20 or 50 gm. of ammoniac sulphate. On this ground the objection is true, owing to the soluble effect exerted by large excess of ammoniacal salts ; but, on the other hand, such excesses are not likely to occur, or must be avoided. Fresenius and Mohr both recommend the process for technical purposes.

If cupric nitrate be used for preparing the solution instead of

sulphate, the presence of baryta, or strontian, or metals precipitable by sulphuric acid, are of no consequence. The solution is standardised by normal nitric or sulphuric acid, and as it slightly alters by keeping, a coefficient must be found from time to time by titrating with normal acid, by which to calculate the results systematically; oxides or carbonates of magnesia, zinc or other admissible metals, are dissolved in excess of normal nitric acid, and titrated residually with the copper solution.

Example : 1 gm. pure oxide of zinc was dissolved in 27 c.c. normal acid, and 2.3 c.c. normal copper solution required to produce the precipitate = 24.7 c.c. acid; this multiplied by the coefficient for monobasic zinc 0.0405, gave 1.001 gm.

3.9 gm. Howard's calcined magnesia was dissolved in 220 c.c. normal sulphuric acid and 30 c.c. copper solution required, whose factor for normal strength was $0.909 = 27.27$ c.c. normal; this deducted from 220, leaves 192.73 c.c. = 3.86 gm. pure magnesia, or 99%. Mother liquors, mixed acids of the galvanic battery containing metals, &c., can be examined for the amount of free acid by this means; so also may acetic acid or vinegar, the only necessary condition being that the acid shall be very dilute, as the copper precipitate is soluble in concentrated cupric acetate; if the first drop of copper solution produces a turbidity which disappears only on shaking or stirring the liquid, the dilution is sufficient; and in order that the first traces of a permanent precipitate may be recognised, it is well to place a piece of dark coloured paper under the beaker. The results are very uniform and reliable.

For the vinegars of commerce this process seems peculiarly applicable, as a large amount of dilution is of no consequence to the reagent, and owing to the colour of malt vinegar, it is of considerable value to the analyst, as it enables him to distinguish the end of the process more exactly.

CARBONIC ACID AND CARBONATES.

§ 23. ALL carbonates are decomposed by strong acids; the carbonic acid which is liberated splits up into water and carbonic anhydride (CO_2), which latter escapes in the gaseous form.

It will be readily seen from what has been said previously as to the estimation of the alkaline earths, that carbonic acid in combination with a great variety of cases can be estimated volumetrically with a very high degree of accuracy.

The carbonic acid to be estimated may be brought into combination with either lime or baryta, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exists in a soluble form as a monocarbonate of alkali, the decomposition is affected by the addition of baric or calcic chlorides as before directed ; if as bicarbonate or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia most frequently contains carbonic acid, it must be removed by the aid of baric or calcic chloride previous to use, should there be any present. It may be kept from absorbing carbonic acid by means of the tube described for normal alkali.

Example: 1 gm. of pure anhydrous sodic carbonate was dissolved in water, precipitated hot with baric chloride, filtered and washed thoroughly with boiling water, the filter and precipitate were then brought into a flask, and 26 c.c. of normal nitric acid added, then titrated with normal alkali, of which 7.2 c.c. were required = 18.8 c.c. of acid ; this multiplied by 0.022, the coefficient for monobasic carbonic acid, gave 0.4136 gm. CO_2 = 41.36 per cent., or multiplied by 0.053, the co-efficient for monobasic sodic carbonic, gave 0.9964 gm. sodic carbonate, instead of 1 gm.

1 gm. of pure and dry sodic bicarbonate in powder was dissolved and precipitated with ammonia and calcic chloride, the precipitate washed with boiling water till all ammonia was removed, the precipitate and filter then titrated with normal acid and alkali ; the quantity of acid used was 23.5 c.c. = 51.7 per cent. of CO_2 ; the percentage, supposing the salt to be absolutely pure, would be 52.3.

There seems to be no difference, with respect to accuracy, between calcic or baric chloride as the precipitant ; but as the calcic carbonate can be more readily washed without clogging the filter, it is preferable to use that substance.

It sometimes occurs that substances have to be examined for carbonic acid, which do not admit of being treated as above described ; such, for instance, as the carbonates of the metallic oxides, (white lead, calamine, &c.), carbonates of magnesia, iron, and copper, the estimation of carbonic acid in cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with calcic chloride, and titrated as before described. The following

form of apparatus (fig. 20) has afforded Mohr the most satisfactory results.

It is the same arrangement in principle as shown in fig. 19 for the distillation of ammonia, with the exception that the flask *b* and tube *d* are somewhat larger, and are placed on a level with the larger flask.

The weighed substance from which the carbonic acid is to be evolved is brought into *b* with a little water and litmus, the tube

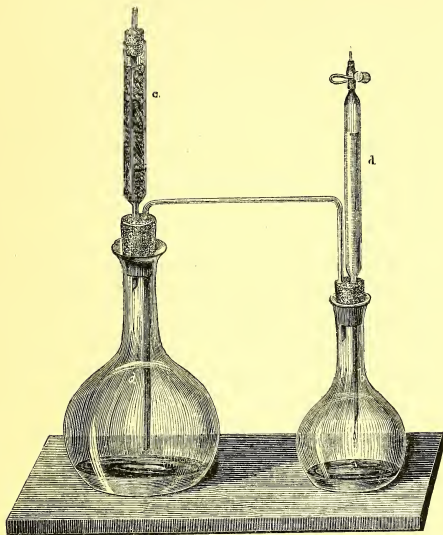


Fig. 20.

d contains strong hydrochloric acid, and *c*, broken glass wetted with ammonia free from carbonic acid. (It should be heated with a little calcic chloride in a test tube; if pure, it will remain clear.) The flask *a* is about one-eighth filled with the same ammonia, the bent tube must not enter the liquid. When all is ready and the corks tight (best secured by wetting them), warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow circumspectly upon the material, which may be heated until all

carbonic acid is apparently driven off, then by boiling and shaking the last traces can be evolved and the operation ended. When cold, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c* so as to carry down any ammonic carbonate that may have formed. Then add solution of calcic chloride, boil, filter, and titrate the precipitate, as before described.

During the filtration, and while ammonia is present, there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

Carbonic Acid Gas in Waters, &c.

Well or spring water, and also mineral waters containing free carbonic acid gas, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of calcic and ammonic chloride, afterwards boiling the mixture, and titrating the precipitate as usual.

Pettenkofer recommends the use of decinormal oxalic acid solution in conjunction with baryta water for the estimation of carbonic acid—using as indicator turmeric paper. Weak solutions of oxalic acid, however, are liable to decomposition on exposure to light, and I therefore prefer hydrochloric or nitric acid. The baryta solution should be preserved in the bottle shown in fig. 17. Lime water may be used instead of baryta with equally good results for very small quantities of carbonic acid.

The principle of the method is that of removing all the carbonic acid from a solution or from a water, by excess of baryta or lime water of a known strength, and after absorption finding the excess of baryta or lime by titration with standard acid.

The following is the best method to be pursued for ordinary drinking waters not containing large quantities of carbonic acid. 500 c.c. of the water are put into a flask with a measured quantity of weak baryta or lime water, the strength of which is previously ascertained by means of decinormal nitric acid, then boiled, well corked, and put aside to cool and settle; when cold and the precipitate subsided, take out 300 c.c. of the clear liquid with a pipette, or pour it off without disturbing the sediment. Let this be titrated with decinormal nitric acid; the quantity required must be calculated for the total water and baryta or lime solution, there being 300 c.c. only taken; the number of c.c. so found must be deducted from the

original quantity required for the baryta solution added; the remainder multiplied by 0.0022 (the acid being decinormal), will give the weight of carbonic acid in the 500 c.c., free and as bicarbonate.

By collecting the precipitate, and titrating it as previously described, the total carbonic acid may be found.

Example: 500 c.c. spring water were mixed with 30 c.c. baryta water = 34.5 c.c. decinormal nitric acid, boiled, corked, and set aside to cool; 300 c.c. of the clear liquid titrated with decinormal acid, of which 6.5 c.c. were required, consequently the 530 c.c. required 11.5 c.c.; this deducted from 54.5 c.c., the quantity required for the 30 c.c. baryta solution, leaves 43 c.c. $\frac{N}{10}$ acid, which multiplied by 0.0022, gives 0.0946 gm. CO_2 , in the 500 c.c. of water, free and as bicarbonate.

The precipitate required 8.4 c.c. normal nitric acid = 0.1848 gm. CO_2 , which is the total weight combined and free; consequently the following calculation will give the results in detail.

Total CO_2	0.1848 gm.
Deduct free and as bicarbonate	0.0946 ,,
	<hr/>
Leaving combined ...	0.0902 ,,

The weight of CO_2 , as bicarbonate, will, of course be equal to this, and the two = 0.1804 gm., which deducted from 0.1848 gm., gives—

Free CO_2	0.0044 gm.
Do. as bicarbonate	0.0902 ,,
Do. as neutral carbonate	0.0902 ,,
	<hr/>
Total.....	0.1848 ,, CO_2 .

If the water contains magnesia, some solution of ammoniac chloride must be added to prevent its precipitation by the baryta; and instead of boiling, which would decompose and dissipate the ammonia, the flask should be closely stoppered and digested in hot water; when perfectly cold and clear the examination may be completed as above. If it be desirable to ascertain the volume of carbonic acid from the weight, 1000 c.c. of gas, at 0° and 0.76 mm., weigh 1.96663 gm. 100 cubic inches weigh 47.26 grains.

For ascertaining the quantity of carbonic acid in bottled aerated waters, such as soda, seltzer, potass, and others, the following appa-

tus is useful. Fig. 21 is a brass tube made like a corkborer about five inches long, having four small holes, two on each side, at about two inches from its cutting end the upper end is securely connected with the bent tube from the absorption flask (fig. 22,) by means of a vulcanised tube; the flask contains a tolerable quantity of



Fig. 21.

Fig. 22.

pure ammonia into which the delivery tube dips; the tube *a* contains broken glass moistened with ammonia.

Everything being ready, the brass tube is greased with tallow or paraffin, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork by turning the bottle round, until

the holes appear below the cork and the gas escapes into the flask. When all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can be possibly eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also; the whole is then precipitated with calcic chloride and boiled, and the precipitate titrated as usual. This gives the total carbonic acid free and combined.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of carbonic acid in the monocarbonate deducted from the total will give the weight of gas originally present.

The volume may be found as follows :—1000 c.c. of carbonic acid at 0°, and 76 mm., weigh 1.966 gm. Suppose, therefore, that the total weight of carbonic acid found in a bottle of ordinary soda water was 2.8 gm., and the weight combined with alkali 0.42 gm., this leaves 2.38 gm. CO² in a free state—

$$1.966 : 2.38 :: 1000 : x = 1210 \text{ c.c.}$$

If the number of c.c. of carbonic acid found is divided by the number of c.c. of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. In this case the contents of the bottle were ascertained by marking the height of the fluid previous to making the experiment ; the bottle was afterward filled to the same mark with water, emptied into a graduated cylinder, and found to measure 292 c.c., therefore

$$\frac{1210}{292} = 4.14 \text{ vols. CO}^2.$$

ESTIMATION OF COMBINED ACIDS IN NEUTRAL SALTS.

§ 24. This comprehensive method of determining the quantity of acid in neutral compounds (but not the nature of the acid), is applicable only in those cases where the base is perfectly precipitated by an excess of caustic alkali or its carbonate. The number of bodies capable of being so precipitated is very large, as has been proved by the researches of MM. Langer and Wawnikiewicz, (*Ann. der Chemie und Pharm.*, p. 239, Feb. 1861), who seem to have worked out the method very carefully. These gentlemen attribute its origin to Bunsen ; but it does not seem certain who devised it. The best method of procedure is as follows :—

The substance is weighed, dissolved in water in a 300 c.c. flask, heated to boiling or not, as may be desirable, then adding, from a burette, normal alkali or its carbonate, according to the nature of the base, until the whole is decidedly alkaline. Dilute to 300 c.c. and put aside to settle ; 100 c.c. are then taken out and titrated for the excess of alkali ; the remainder multiplied by 3, gives the measure of the acid combined with the original salt, *i.e.*, supposing the precipitation is complete.

Example : 2 gm. crystals of baric chloride were dissolved in water, heated to boiling, and 20 c.c. normal sodic carbonate added, diluted to 300 c.c., and 100 c.c. of the clear liquid titrated with normal nitric acid, of which 1.2 c.c. were required—altogether, therefore, the 2 gm. required 16.4 c.c. normal alkali ; this multiplied by 0.122, gave 2.0008 gm. Ba Cl, instead of 2 gm. ; multiplied by the factor for chlorine 0.03546, it yielded 0.58154 gm., theory requires 0.5813 gm. chlorine.

The following substances have been submitted to this mode of examination with satisfactory results :—

Salts of the alkaline earths precipitated, boiling hot, with an alkaline carbonate.

Salts of magnesia, with pure or carbonated alkali.

Alum, with carbonate of alkali.

Zinc salts, boiling hot, with the same.

Copper salts, boiling hot, with pure potash.

Silver salts, with same.

Bismuth salts, half-an-hour's boiling, with sodic carbonate.

Nickel and Cobalt salts, with same.

Lead salts with the same.

Iron salts, boiling hot, with pure or carbonated alkali.

Mercury salts, with pure alkali.

Protosalts of manganese, boiling hot, with sodic carbonate.

Chromium persalts, boiling hot, with pure potash.

Where the compound under examination contains but one base precipitable by alkali, the determination of the acid gives, of course, the quantity of base also.

Wolcott Gibbs (Chem. News, vol. i., 1868, p. 151) has enunciated a new acidimetric principle applicable in cases where a base is precipitable at a boiling temperature by hydric sulphide, and the acid set free so as to be estimated with standard alkali. Of course the method can only be used where complete separation can be obtained, and where the salt to be analysed contains a fixed acid which has no effect upon hydric sulphide. A weighed portion is dissolved in water brought to boiling, and the gas passed in until the metal is completely precipitated, known by testing a drop of the clear liquid upon a porcelain tile with sulphuretted hydrogen water, or any other appropriate agent adapted to the metallic salt under examination.

The liquid is filtered from the precipitate, and the latter well washed, and the solution made up to a definite measure. An aliquot portion is then titrated with normal alkali and litmus as usual.

In the case of nitrates or chlorides, where nitric or hydrochloric acid would interfere with the hydric sulphide, it was found that the addition in tolerable quantity of a neutral salt containing an organic acid (*e.g.*, sodic or potassic tartrate, or the double salt) obviated all difficulty.

The results obtained by Gibbs in the case of copper, lead, bismuth, and mercury, as sulphate, nitrate, and chloride, agreed very closely with theory; but the process would be very objectionable

to many on account of the offensive and poisonous character of the gas necessarily employed in the precipitation.

ESTIMATION OF SULPHURIC ACID, BARYTA, CHLORINE, IODINE, AND BROMINE INDIRECTLY.

§ 25. BOHLIG (Fresenius' Zeitschrift, 1870, p. 310) has described a method for estimating these bodies, which appears worthy of some consideration, since the only standard solutions required are an acid and an alkali.

In the case of sulphates of the alkalies the principle is as follows :—

Barytic carbonate and carbonic acid in the form of alkaline monocarbonate, added to a hot solution of alkaline sulphate, produce barytic sulphate and acid carbonate of alkali, the latter in proportion to the sulphuric acid present. The titration of the excess of alkali gives the amount of sulphuric acid.

With baryta, of course, the same principle applies. Neutral salts of iodine, chlorine, and bromine with alkalies (except ammonia) in solution, with the addition of moist argentic oxide, quickly produce the respective compounds of silver, setting free an equivalent amount of free alkali, which can be titrated as before.

The author also claims for the process the merit of estimating mixed soda and potash as sulphates.

I merely indicate the nature of the method here, not having had time to investigate it in detail, but refer to the paper quoted above.

PART III.

ANALYSIS BY OXIDATION OR REDUCTION.

INTRODUCTION.

§ 26. THE series of analyses which occur under this system are very extensive in number, and not a few of them possess extreme accuracy, such, in fact, as is not possible in any analysis by weight, consequently they have now been established, whenever practicable, instead of the old system. The completion of the various processes is generally shown by a distinct change of colour—such, for instance, as the occurrence of the beautiful rose red permanganate, or the blue iodide of starch; and as the smallest quantity of these substances will colour distinctly large masses of liquid, the slightest excess of the oxidising material is sufficient to produce a satisfactory result.

The principle involved in the processes is extremely simple. Substances which will take up oxygen are brought into solution, and titrated with a substance of known oxidising power—such, for instance, as occurs in the determination of ferrous salts by permanganic acid. The iron is ready and willing to receive the oxygen, the permanganate is equally willing to part with it; while the iron is absorbing the oxygen, the permanganate loses its colour almost as soon as it is added, and the whole mixture is colourless, but immediately the iron is satisfied, the rose colour no longer disappears, there being no more oxidisable iron present. 1 atom FeO absorbs 1 atom oxygen, becoming 1 atom Fe^2O^3 . Oxalic acid occupies the same position as the ferrous salts, its composition is $\text{C}^2\text{O}^4\text{H}^2 + 2\text{H}^2\text{O} = 126$; if permanganate is added to it in acid solution, the oxalic acid is oxidised to carbonic acid, and the manganic reduced to manganous oxide, thus $\text{Mn}^4\text{O}^7 + 5\text{C}^2\text{O}^4\text{H}^2 + 2\text{H}^2\text{SO}^4 = 10\text{CO}^2 + \text{Mn}2\text{SO}^4 + 7\text{H}^2\text{O}$; when the oxalic acid is all decomposed the colour of the permanganate no longer disappears. On the other hand, substances which will give up oxygen are deoxidised by a known excessive quantity of reducing agent, the amount of which excess is afterwards ascertained by residual titration with a standard

oxidising solution; the strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The oxidising agents best available are—potassic permanganate, iodine, potassic bichromate, and red potassic prussiate.

The reducing agents are—sulphurous acid, sodic hyposulphite, oxalic acid, ferrous oxide, arsenious anhydride, stannous chloride, yellow potassic prussiate and zinc.

With this variety of materials a great many combinations may be arranged so as to make this system of analysis very comprehensive, but the following are given as sufficient for almost all purposes, and as being susceptible of the greatest amount of purity and stability of material, with exceedingly accurate results:—

1. Permanganate and ferrous salts (with the rose colour as indicator); permanganate and oxalic acid (with the rose colour as indicator).

2. Potassic bichromate and ferrous salts (with cessation of blue colour when brought in contact with red potassic prussiate, as indicator).

3. Iodine and sodic hyposulphite (with starch as indicator); iodine and sodic arsenite (with starch as indicator).

PREPARATION OF STANDARD SOLUTIONS.

PERMANGANIC ACID AND FERROUS OXIDE.

1. Potassic Permanganate.

$K^2 Mn^2 O^8 = 316$. Decinormal Solution = 3.16 gm. per litre.

§ 27. THE solution of this salt is best prepared for analysis by dissolving the pure crystals in distilled water of such a strength that 17.85 c.c. will peroxidise 1 decigramme of iron. The solution is then decinormal. If well kept, it holds its strength several months.

If the salt can be had perfectly pure and dry, 3.16 gm. dissolved in a litre of water at 16° C. will give an exactly decinormal solution; but, nevertheless, it is always well to titrate it upon a definite quantity of iron or oxalic acid.

A very useful form of bottle for preserving it is that shown in fig. 17. Burettes can then be filled with the solution without its

frothing. The cork in the tubulure must, however, be well soaked in melted paraffine.

The solution may also be kept in any good stopped bottle, and while it is quite free from sediment, it may be taken for granted that its strength is unaltered.

2. Titration of Permanganate with Ferrous Ammonia Alum.

In order to ascertain the strength of the permanganate it must be titrated with either a weighed quantity of metallic iron, oxalic acid, or the double sulphate of iron and ammonia.

This latter salt is a most convenient substance for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and being perfectly stable when pure, it can be depended on without risk. To prepare it, 139 parts of the purest crystals of ferrous sulphate, and 66 parts of pure crystallised ammonic sulphate are separately dissolved in the least possible quantity of distilled water of about 40° C., if the solutions are not perfectly clear they must be filtered; mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold, during the stirring the double salt will fall in a finely granulated form, set aside for a few hours, then pour off the supernatant liquor, and empty the salt into a clean funnel with a little cotton wool stuffed into the neck; so that the mother liquor may drain away, the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper, or still better, as Mohr recommends, dried in a centrifugal machine. As very few persons are possessed of this latter, albeit a most useful article, the salt may be spread out on a tray made of filtering paper, and the superfluous moisture driven off by a fan or pair of bellows; lastly, place it in a current of air to dry thoroughly so that the small grains adhere no longer to each other or to the paper in which they are contained, then preserve in a stoppered bottle for use. It is constantly being stated in books that this salt does not keep of uniform constitution—if so it simply arises from imperfect preparation. If thoroughly dried in air at ordinary temperatures so that the grains do not adhere to each other when placed in a bottle or on paper—it remains the same for years.

The formula of the salt is— $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} = 392$.

Consequently it contains exactly one-seventh of its weight of iron, therefore, 0.7 gm. represent 0.1 gm. of iron, and this is a convenient quantity to weigh for the purpose of titrating the permanganate, or

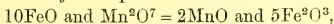
an exact decinormal solution may be made by dissolving 39.2 gm. in a litre of water with the addition of 10 c.c. pure sulphuric acid, and preserving in the bottle (fig. 17).

0.7 gm. being brought into dilute solution in a flask or beaker, and 5 or 6 c.c. of dilute sulphuric acid (1 to 5) added, (the titration of permanganate, or any other substance, by it should always take place in the presence of free acid and preferably sulphuric), the permanganate is delivered from a Gay Lussac's burette or the burette with glass tap divided in $\frac{1}{5}$ or $\frac{1}{10}$ c.c., until a point occurs, when the rose colour no longer disappears on shaking; a few drops of the permanganate in excess are sufficient to produce this effect, but the actual quantity required to colour the same quantity of water should be found, and deducted from the total used in the analysis. The titration is now ended, and should the quantity not be strictly correct, the number of c.c. used may be marked upon the bottle as the quantity for 0.1 gm. Fe, or the factor found, which is necessary to reduce it to decinormal strength, or diluted to that strength at once.

3. Titration with Metallic Iron.

The purest iron to be obtained is the thin annealed binding-wire free from rust. About 0.1 gm. of this is to be dissolved in dilute sulphuric acid by the aid of heat, in a small flask closed with a cork, through which a fine glass tube is passed, so that the hydrogen which is evolved escapes under pressure, thus preventing the access of air; or better than this, the plan suggested by Mohr may be used, which consists in passing the upper end of the fine tube through a cork; over the end of the glass tube, which is level with the cork, a small piece of sheet india rubber or oiled silk is laid and pinned down to the cork with a pin on each side of the hole. This contrivance acts as a valve by which the hydrogen escapes from the flask under pressure, but so soon as the pressure of gas ceases and the flask cools, the valve closes by atmospheric pressure and thus prevents the entrance of air; by this means there is no difficulty in obtaining the whole of the iron in solution as protoxide. When the iron is all dissolved the flask may be two-thirds filled with cold distilled water, and the titration with permanganate commenced and concluded as in the case of the double sulphate. See also § 39. 6.

The decomposition which ensues from treating ferrous oxide by permanganic acid may be represented as follows:—



therefore 1 atom ferrous oxide absorbs 1 atom of oxygen and is changed into 1 atom ferric oxide.

4. Titration with Oxalic Acid.

0.63 gm. of the pure acid is to be weighed, or 10 c.c. of normal solution measured with a pipette, brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 58° C., and the permanganate added from the burette. The colour disappears slowly at first but afterward more rapidly, becoming first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid, nevertheless, it is as reliable with care and attention.

5. Precautions.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting manganous oxide in solution. Sulphuric acid, in a dilute form, has no prejudicial effect on the pure permanganate, even at a high temperature; not so, however, nitric or hydrochloric acids, the former, though very dilute, if it contain the lower oxides of nitrogen, immediately decomposes the solution, consequently the last traces of these must be removed by boiling previous to its addition. With hydrochloric acid the solution to be titrated must be very dilute and of low temperature, otherwise chlorine will be liberated and the analysis spoiled; this acid acting as a reducing agent on permanganate in concentrated solution, thus



under any circumstances the analysis must be subjected to correction with this acid, as will be shewn further on.

Organic matter of any kind decomposes the permanganate, and the solution, therefore, cannot be filtered through paper, nor can it be used in Mohr's burette, because it is decomposed by the india rubber tube.

The determination of iron by permanganate, under many circumstances hitherto recommended, is subject to great error, so great an error in fact, that the determination may be totally worthless unless subjected to correction.

In Fresenius' "Zeitschrift für Analytische Chemie," part 3, (pub. in Oct. 1862.) Löwenthal and Lenssen have contributed

a valuable paper on the subject, a short summary of which is as follows. A complete series of determinations of iron were made with different quantities of free hydrochloric and sulphuric acids, with variable quantities of water, free from air and containing air and at various temperatures, correction being in all cases made for the quantity of solution of permanganate necessary to colour the various bulks of liquid.

The results proved conclusively that the process was exact only when the iron existed as sulphate, when a moderate quantity of free sulphuric acid was present, and when deduction was made for the coloration of the liquid. Fresenius has also most carefully checked the statements made by Löwenthal and Lenssen, obtaining results which points to the same conclusion. It is not necessary to give the experiments of Fresenius in detail. The permanganate solution was prepared with the pure crystals of such strength that 100 c.c. = 0.4 gm. iron. The iron solution was prepared from pure sulphate. The hydrochloric and sulphuric acids used were absolutely pure, the first 1.12 spec. grav., the last 1.23; fresh distilled water was used for the dilution, and in order to remove any traces of reducing agents it was acidified with sulphuric acid, and sufficient permanganate added to give a permanent pinkish colour. The correction, therefore, for coloration of the liquid was unnecessary.

The variation in quantity of permanganate required for 10 c.c. iron solution was from 12.6 to 14.3 c.c., the difference being in all cases larger with the increase of hydrochloric acid.

From these experiments it is proved that titration with permanganate is far less reliable in the presence of free hydrochloric than sulphuric acid, owing, undoubtedly, to the reaction previously explained. All researches, however, go to prove that when a solution of the substance to be titrated with hydrochloric acid is divided into three portions, and successively titrated in the same liquid, the mean of the second and third (setting the first entirely aside), will be dependable.

There can be very little doubt that the discrepancies shewn to occur in the use of hydrochloric acid will account, in some measure, for the frequent want of accuracy in Pelouze's method for the determination of nitrates and similar processess. It is, therefore, advisable, in all possible cases, to use sulphuric acid for acidifying the solution and to avoid any large excess.

Where hydrochloric acid must be used and potassic bichromate is not admissible for titration, the fractional estimation before-

mentioned must be adopted, taking the second, or mean of second and third titrations as correct; where this is not practicable it is best to prepare a mixture of hydrochloric acid and water, add some ferrous sulphate, and titrate with permanganate to the red tinge, then add the substance, and titrate with permanganate. Experiment has shown that this method is reliable.

TITRATION OF FERRIC SALTS BY PERMANGANATE.

§ 28. All ferric compounds requiring to be estimated by permanganate must of course be reduced to the ferrous state—this is best accomplished by metallic zinc in sulphuric acid solution—hydrochloric may also be used with due precaution (see § 27. 5).

The reduction may be accomplished by simply adding to the warm diluted solution small pieces of zinc (free from iron, or at least with a known quantity present), until colourless, or until a drop of the solution brought in contact with a drop of potassic sulphocyanide produces no red colour.

The reduction may be hastened considerably either by using a flask containing so much amalgamated zinc in pieces (*i. e.*, zinc saturated with mercury) as to occupy almost as much space as the liquid, or by placing the liquid in a platinum crucible or basin, with small pieces of zinc; in this latter case a galvanic circuit is established, by which the reduction is accomplished with the use of very little zinc, the capsule should be covered with a glass plate or otherwise confined during the operation.

When the reduction is fully obtained, no time should be lost in titrating the solution.

CALCULATION OF ANALYSES MADE WITH PERMANGANATE SOLUTION.

§ 29. The calculation of analysis with permanganate, if the solution is not strictly decinormal, can be made by ascertaining its constant factor, reducing the number of c.c. used of it to decinormal strength, and multiplying the number of c.c. thus found by $\frac{1}{100000}$ of the atom. wt. of the substance sought; for instance—

Suppose that 15 c.c. of permanganate solution have been found to equal 0.1 gm. iron, it is required to reduce the 15 c.c. to decinormal strength, which would require 1000 c.c. of permanganate to every 5.6 gm. iron, therefore $5.6 : 1000 :: 0.1 x = 17.85$ c.c.; $17.85 \times 0.0056 = 0.09996$ gm. iron, which is as near to 0.1 gm. as can be

required. Or the factor necessary to reduce the number of c.c. used may be found as follows:— $0.1 : 15 :: 56 : x = 84$ c.c., therefore, $\frac{100}{84} = 1.19$. Consequently 1.19 is the factor by which to reduce the number of c.c. of that special permanganate used in any analysis to the decinormal strength, from whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result:—

$$\begin{array}{ccccccc} 1 \text{ at. Fe (56)} & & \text{at weight of} & & \text{the weight} & & \text{the weight of} \\ & & \text{the substance} & :: & \text{of Fe or} & & \text{substance} \\ & \text{or} & & & & & \\ 1 \text{ at. } \overline{\text{O}} \text{ (63)} & & \text{sought} & & \overline{\text{O}} \text{ found} & & \text{sought.} \end{array}$$

taken as monobasic.

In other words, if the atomic weight of the substance analysed be divided by 56 or 63 (the respective atomic weights of iron or oxalic acid), a factor is obtained by which to multiply the weight of iron or oxalic acid, equal to the permanganate used, the product is the weight of the substance analysed.

For example, copper is the substance sought, 1 at. Cu corresponding to 1 at. Fe is 63.5, let this number, therefore, be divided by 56, whence $\frac{63.5}{56} = 1.134$, therefore, if the quantity of iron represented

by the permanganate used in a copper analysis be multiplied by 1.134, the product will be the weight of the copper sought.

Again, in the case of manganic peroxide whose monobasic atomic weight is 43.5,

$$\frac{43.5}{56} = 0.7768,$$

the weight of iron therefore found by permanganate in any analysis multiplied by the factor 0.7768, will give the amount of manganic peroxide, MnO^2 . Again, if m gm. iron = k c.c. permanganate, then

$$1 \text{ c.c. permanganate} = \frac{m}{k} \text{ metallic iron.}$$

Where possible the necessary factors will be given in the tables preceding any leading substance.

CHROMIC ACID AND FERROUS OXIDE.

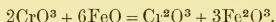
1. Potassic Bichromate.

$\text{Cr}^2\text{O}^7\text{K}^2 = 295$, Decinormal solution = 4.917 gm. per litre.

§ 30. This substance, which appears to have been first proposed

by Penny, possesses the advantage over permanganate, that it is absolutely permanent in solution, may frequently be obtained in ordinary commerce in a pure state; beside which, its solution may be used in Mohr's burette without undergoing the change peculiar to permanganate; on the other hand, the end of the reaction in the estimation of iron can only be known by an external indicator, that is to say, a drop of the mixture is brought in contact with a drop of solution of red potassic-prussiate (freshly prepared) upon a white slab or plate; while the ferrous oxide is in tolerable excess, a rich blue colour occurs at the point of contact between the drops, but as this excess continues to lessen by the addition of the bichromate, the blue becomes somewhat turbid, having first a green, then grey, and lastly brown shade. When the greenish blue tint has all disappeared, the process is finished. This series of changes in the colour admits of tolerably sure reading of the burette, after some little practice is obtained.

The reaction between chromic acid and ferrous oxide may be represented by the formula,



The decomposition takes place immediately, and at ordinary temperatures, in the presence of free sulphuric or hydrochloric acid; nitric acid is of course inadmissible.

The reduction of ferric compounds to the ferrous state may be accomplished by zinc or sulphurous acid as with permanganate; or, instead of these, stannous chloride may be used, which acts very rapidly as a reducing agent upon ferric oxide, the yellow colour of the solution disappearing almost immediately.

In the analysis of iron ores this method of reduction is serviceable; the greatest care, however, is necessary that the protochloride is not present in excess, as this would consume the bichromate solution equally with the protoxide of iron, and so lead to false results.

The discharge of the yellow colour of the iron solution may with care be made a very sure indication of the exact point of reduction. The concentrated hydrochloric solution of iron is heated to gentle boiling, and the moderately dilute tin solution added with a pipette, waiting a moment after each addition till the last traces of colour have disappeared; the solution is then poured into a beaker, diluted with water, and titrated with the bichromate as usual; an extra security is obtained by adding a few drops of potassic sulphocyanide

to the solution, the disappearance of the blood-red colour indicating that no more ferric oxide is present.

In order to obviate the inaccuracy which would be produced by an excess of tin in the state of protosalt, Mohr recommends that chlorine water should be added by drops to the mixture until a rod moistened with it and brought in contact with blue iodide of starch paper no longer removes the colour, the excess of stannous chloride is then all converted into stannic chloride, and the titration with bichromate may proceed as usual. For the direct titration of iron by stannous chloride see § 41.

It is absolutely necessary that the solution of potassic ferridecyanide used as the indicator with bichromate should be free from ferrocyanide; and as a solution when kept for some little time becomes in some measure converted into the latter, it is best to use a freshly-prepared liquid, or at least to test the indicator with a persalt of iron previous to titration.

2. Preparation of the Decinormal Solution of Bichromate.

4.917 gm. per litre.

As 1 atom of potassic bichromate gives up 3 atoms of oxygen, it is necessary that $\frac{1}{6}$ th at. in grammes should be used for the litre as a normal solution, and $\frac{1}{60}$ th for the decinormal; and as it is preferable on many accounts to use a dilute solution, the latter is the most convenient for general purposes.

According to the latest and most reliable researches, the equivalent number of chromium is 52.5, and consequently that of potassic bichromate is 295; if, therefore, $\frac{1}{60}$ th of this latter number = 4.917 gm. be dissolved in a litre of water, the decinormal solution is obtained. On the grain system, 49.17 grains to 10,000 grains of water will give the same solution.

1 c.c. or 1 dm. of this solution is capable of yielding up $\frac{1}{10000}$ at. in grammes of oxygen, and is therefore equivalent to the $\frac{1}{10000}$ at. of any substance which takes up 1 atom of oxygen.

3. Solution of Stannous Chloride.

About 6 gm. pure tin in thin pieces (not the commercial tin-foil containing lead) is put into a large platinum capsule, and about 200 c.c. strong hydrochloric acid poured over it, and heated till dissolved; or it may be dissolved in a porcelain capsule or glass flask, adding pieces of platinum foil to excite a galvanic current. The

solution so obtained is diluted to about a litre with pure fresh distilled water, and preserved in the bottle (fig. 17), or in any other well-closed vessel.

Its strength alters slightly from day to day, however well kept, and consequently it must be titrated for each day's use with $\frac{N}{10}$ iodine and starch, as in § 31. 4.

4. Examples of Analysis.

0.7 gm. of pure and dry double sulphate of iron and ammonia = 0.1 gm. iron, was dissolved in about 2 oz. of water and titrated with decinormal bichromate, of which 17.85 c.c. were required; this multiplied by 0.0392 gave 0.699 gm. instead of 0.7 gm.

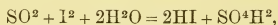
0.56 gm. of iron wire required 99.8 c.c. = 0.5588 gm.; as it is impossible to obtain iron wire perfectly pure, the loss is undoubtedly owing to the impurities.

If the bichromate solution should from any accidental cause be found not strictly of decinormal strength, the factor necessary for converting it must be found as previously described.

As it is not at all an uncommon occurrence, in an analysis where no sign of the end of the reaction is visible in the solution itself, to overstep the exact point, it is advisable to have some method of bringing it into order again; this may be accomplished in the present case by adding a definite quantity of the double iron salt to the mixture, titrating afresh, and deducting the proportional amount of bichromate from the total quantity required.

IODINE AND SODIC HYPOSULPHITE.

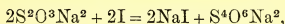
§ 31. THE principle of this now beautiful and exact method of analysis was first discovered by Dupasquier, who used a solution of sulphurous acid instead of sodic hyposulphite. Bunsen improved his method considerably by ascertaining the sources of failure to which it was liable, and which consisted in the use of a too concentrated solution of sulphurous acid; the reaction between iodine and very dilute sulphurous acid may be represented by the formula:—



if the sulphurous acid is more concentrated, *i.e.*, above 0.04 per cent in a short time, the action is reversed, the irregularity of decomposition varying with the quantity of water present, and the rapidity with which the iodine is added. Under proper regulations, there-

fore, we see that free iodine converts sulphurous into sulphuric acid by decomposing water, the oxygen of which goes to the sulphurous, and produces sulphuric acid ; the hydrogen is taken by the iodine, forming hydriodic acid.

There are great drawbacks, however, connected with the use of sulphurous acid ; it very rapidly changes by keeping even in the most careful manner, so much so, that a sample tested in the morning would very frequently need an examination in the afternoon ; and as it must be exceedingly dilute, it necessitates the use of special vessels and burettes. Taking all these things into account, therefore, the substitution of sodic hyposulphite is a great advantage, inasmuch as the end is secured quite as accurately without the trouble and insecurity connected with the sulphurous acid. The reaction in the case of sodic hyposulphite is as follows :—



the result being that hyposulphurous acid takes oxygen from the water, with the production of tetrathionic and hydriodic acids in combination with soda.

In order to ascertain the end of the reaction in analysis by this method an indicator is necessary, and the most delicate and sensitive for the purpose is starch, which produces with the slightest trace of free iodine in cold solution the well-known blue colour of iodide of starch. Hydriodic acid or iodides have no influence upon the colour.

The principle of this method, namely, the use of iodine as an indirect oxidising body by its action upon the elements of water, forming hydriodic acid with the hydrogen, and liberating the oxygen in an active state, can be applied to the determination of a great variety of substances with extreme accuracy.

The stability of sodic hyposulphite, and the ease with which it may be obtained in a pure state, enable the standard solutions to be prepared and kept for some time of proper systematic strength.

Bodies which take up oxygen, and decolorise the iodine solution, such as sulphurous acid, sulphites, sulphuretted hydrogen, alkaline hyposulphites and arsenites, stannous chloride, &c., are brought into dilute solution, starch liquor added, and the iodine delivered in with constant shaking or stirring until a point occurs at which a final drop of iodine colours the whole blue—a sign that the substance can take up no more iodine, and that the drop in excess has shown its characteristic effect upon the starch.

Free chlorine, or its active compounds, cannot, however, be titrated

with hyposulphite direct, owing to the fact that, instead of tetrathionic acid being produced as with iodine, sulphuric acid occurs, as may be readily seen by testing with baric chloride. In such cases, therefore, the chlorine must be evolved from its compound into an excess of solution of pure potassic iodide, where it at once liberates its equivalent of iodine, which can then, of course, be estimated with hyposulphite.

All bodies which contain available oxygen, and which evolve chlorine when boiled with strong hydrochloric acid, either atom for atom, or in some other definite relation, such as the chromates, manganates, and all metallic peroxides, can readily and most accurately be estimated by this method.

1. Preparation of the Decinormal Solution of Iodine,

I = 127 ; 12·7 gm. per litre.

Chemically pure iodine may be obtained by mixing commercial iodine with about one-fourth of its weight of potassic iodide, and gently heating the mixture between two large watch-glasses or porcelain capsules, the lower one being placed upon a heated iron plate, the iodine sublimes in brilliant plates which are absolutely pure, the re-sublimed iodine of commerce is not always free from chlorine, it is therefore sometimes necessary to prepare it specially by a second sublimation as described above.

The watch-glass or capsule containing the iodine is placed under the exsiccator to cool, and also to deprive it of any traces of watery vapour ; then 12·7 gm. ($= \frac{1}{10}$ at.) accurately weighed, and together with about 18 gm. of pure white potassic iodide dissolved in about $\frac{1}{4}$ litre of water, then diluted to exactly 1 litre. The same solution may be obtained by dissolving 127 grains of iodine, and 180 of potassic iodide, in 10,000 grains of water ; in either case the solution is strictly decinormal ; the flask must not be heated in order to promote solution, and care must be taken that iodine vapours are not lost in the operation.

The solution is best preserved in stoppered bottles of about 5 or 6 oz. capacity, which should be completely filled.

2. Decinormal Sodid Hyposulphite.

24·8 gm. per litre.

As 1 atom of this salt absorbs 1 atom of iodine or oxygen, it is requisite that $\frac{1}{10}$ at. in grammes of the pure salt should be

contained in the litre, and as 248 is the equivalent number of the salt, 24.8 gm. is the quantity to be weighed. As it is not difficult either to manufacture or procure pure sodic hyposulphite, this quantity, powdered and dried between blotting paper, may be weighed direct, and dissolved in a litre of distilled water, and then titrated with the iodine solution and a little starch liquor. If impure hyposulphite should have been used, or the sample not entirely free from accidental moisture, it will be necessary to find a factor by which to reduce it to decinormal strength, as described for previous solutions, or the amount of impurity being known, a fresh quantity may be prepared of proper strength. It is advisable to preserve the solution in the dark. After a time all solutions of hyposulphite undergo a slight amount of oxidation, and sulphur deposits upon the bottle, it is therefore always advisable to examine previous to use.

Beside the decinormal iodine and hyposulphite, it is convenient in some cases to use centinormal solutions, which can readily be prepared by diluting 100 c.c. of each decinormal solution to 1 litre.

In using the iodine solution, Mohr's burette may be employed, but care must be taken that the solution is not left in it for any length of time, as decomposition slowly takes place, and the tube becomes hard; Gay Lussac's, or the tap burette, are on this account preferable.

3. Starch Liquor.

1 part of clean arrowroot, potato, wheat, rice, sago, or other starch, is first mixed smoothly with cold water into a paste, and about 150 or 200 times its weight of boiling water poured over it, and allowed to stand and settle; the clear liquor only is to be used as the indicator, of which a few drops only are necessary. As the liquor so prepared does not keep long, and is not near so sensitive when old, several methods have been devised for the purpose of preserving it. Pure glycerine added to the clear solution in proportion of one-tenth of its volume answers very well. Flückiger recommends:—1 part of starch to be well shaken and digested in a bottle with about 15 parts of a solution of calcic chloride, containing half its weight of the salt; when the mixture appears slimy and fibrous, showing that the starch granules are broken, it is largely diluted with water, say to about 250 times its volume, it may then be allowed to settle, or is filtered, and the clear liquor saturated with common salt, then preserved in a cool place for use.

Neither of these methods, however, are so reliable as the freshly prepared solution.

4. Example of Titration.

A crystal of pure sodic hyposulphite weighing 0.634 gm. was dissolved in distilled water, starch added, and 127.2 c.c. iodine solution of unknown strength required to produce the blue colour, since the $\frac{N}{10}$ hyposulphite should contain 24.8 gm. per litre, the quantity of iodine solution, if rigidly decinormal, should be

$$24.8 : 1000 = 0.634 : \frac{0.634}{24.8} = 25.56 \text{ c.c.};$$

but the quantity actually used was 27.2 c.c. ; the coefficient therefore is

$$27.2 \times 25.56, \text{ whence, } x \frac{25.56}{27.2} = 0.94.$$

Since decinormal bichromate solution is very permanent, it is a very exact and convenient agent for titrating the strength of a hyposulphite solution as follows:—

Let a convenient quantity, say 20 c.c. of bichromate to be measured into a stoppered flask, adding solution of pure potassic iodide in sufficient excess to keep the liberated iodine in solution, then add hydrochloric acid about 5 c.c. and shake together for a few minutes until the decomposition is complete, now add starch and titrate with hyposulphite until colourless, the number of c.c. of bichromate divided by that of the hyposulphite will give the coefficient necessary for correcting the hyposulphite to $\frac{N}{10}$ strength.

ANALYSIS OF SUBSTANCES BY DISTILLATION WITH HYDROCHLORIC ACID.

§ 32. THERE are a great variety of substances containing oxygen, which when boiled with hydrochloric acid, yield chlorine, equivalent to the whole or a part only of the oxygen they contain according to circumstances. Upon this fact are based the variety of analyses which may be accomplished by means of iodine and sodic hyposulphite; the chlorine so evolved, however, is not itself estimated, but is conveyed by means of a suitable apparatus into a solution of potassic iodide, thereby liberating an equivalent quantity of iodine. This latter body is then estimated by hyposulphite; the quantity so found is, therefore, a measure of the oxygen existing in the original substance,

and consequently a measure of the substance itself. It seems a very roundabout method, and one would imagine it could scarcely lead to accurate results ; nevertheless, without exaggeration, it may be said to be the most exact in the whole range of volumetric analyses, far outstripping any process of analysis by weight.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkaline iodide, may possess a variety of forms,—the most serviceable, however, being the three kinds devised respectively by Bunsen, Fresenius, and Mohr.

Bunsen's consists of a small flask to contain the mixture for distillation, connected by a stout piece of vulcanized tubing with a long bent tube, which is carried into the solution of iodide contained in an inverted retort, the neck of the latter having a tolerably large bulb blown midway, so that when the chlorine is all evolved from the mixture, and hydrochloric acid gas begins to distil, the rapid condensation which ensues may not cause the liquid to rush back to the flask, and so spoil the operation. This unavoidable regurgitation is a great nuisance, and in order to prevent the entrance of the liquid into the bent tube, Bunsen contrived a little self-acting valve, which consists of a very light glass bulb with a stalk (very like the large headed ornamental pins used by ladies for their hair) ; this presents no hindrance to the evolution of the gas during the distillation, but when the liquid attempts to enter, the bulb is forced up to the end of the delivery tube, so as to close the entrance ; a drawing of the entire apparatus may be seen in most treatises on chemical analysis.

A far better preventive of this regurgitation is, however, suggested by Fresenius, and applicable to each kind of apparatus—namely, the addition of a few pieces of pure magnesite (native magnesic carbonate) ; this substance dissolves but slowly in the hydrochloric acid, and so keeps up a constant flow of carbonic acid gas, whose pressure is sufficient to prevent the return of the liquid.

The apparatus contrived by Fresenius differs from Bunsen's only in having two large bulbs blown in the neck of the retort, and one in the bent delivery tube.

Mohr's apparatus is shown in fig. 23, and is, on account of its simplicity of construction, very easy to use.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffin ; through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely into a stout tube about 12 or 13 inches

long and 1 inch wide, closed at one end like a test tube ; this tube, containing the alkaline iodide, is placed in an ordinary hydrometer

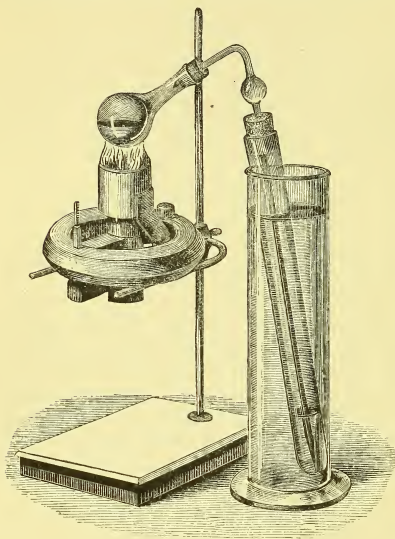


Fig. 23.

glass, about twelve inches high, and surrounded by cold water ; the delivery tube is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the tall hydrometer glass keeps everything in position. The substance to be distilled is put into the flask and covered with strong hydrochloric acid, the magnesite added, the condenser supplied with a sufficient quantity of iodide solution,

and the apparatus put together tightly ; either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at pleasure ; in the case of the common spirit lamp, it may be held in the hand, and applied or withdrawn according to the necessities of the case ; the argand spirit or gas lamp can, of course, be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved, should be more than will remain in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask, and preserved for analysis, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued

for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner previously described.

Instead of the large test tube, some operators use a U tube to contain the potassic iodide, having a bulb in each limb, but the latter is not necessary if magnesite is used.

The solution of potassic iodide may conveniently be made of such a strength that $\frac{1}{16}$ atom or 33.2 gm. is contained in the litre. One cubic centimeter will then be sufficient to absorb the quantity of free iodine, representing 1 per cent. of oxygen in the substance analysed, supposing it to be weighed in system. In examining peroxide of manganese, for instance, 0.436 gm. or 4.36 gm. would be used, and supposing the percentage of peroxide to be about 60, 60 c.c. or dm. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 c.c. or dm. should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine. It may sometimes happen that not enough iodide is present to keep all the liberated iodine in solution—in which case it will separate out in the solid form; more iodide, however, may be added to dissolve the iodine; the titration can then be made as usual.

The process of distillation above described may be avoided in many cases. There are a great number of substances which, by mere digestion with hydrochloric acid and potassic iodide at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to regrind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water, if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 1 to 5 or 6 oz., according to the necessities of the case.

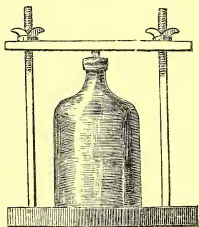


Fig. 24.

The stopper may be secured by fine copper binding wire, or a kind of clamp contrived by Mohr may be used, as shown in fig. 24 ; by means of the thumb screws the pressure upon the stopper may be increased to almost any extent.

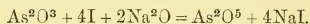
The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of potassic iodide and pure hydrochloric acid added ; the stopper is then inserted, fastened down, and the bottle placed in a saucepan of water with a little tow, or other similar substance, to keep the glass from touching the bottom, and the water then made to boil by a gas flame or hot plate as may be most convenient ; when the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and after being shaken, is opened, emptied into a beaker, and diluted by the washings for titration.

The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation. Many of them even at ordinary temperatures.

The potassic iodide used in the various analyses must be absolutely free from potassic iodate and free iodine.

ARSENIOUS ACID AND IODINE.

§ 33. THE principle upon which this method of analysis is based is the fact, that when arsenious acid is brought in contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being—



The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of carbonate, as pure alkalies interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of sodic carbonate, the blue colour does not occur until all the arsenious acid is oxidised into arsenic acid ; in like manner, a standard solution of arsenious acid may be used for the estimation of iodine or other bodies which possess the power of oxidising it.

The chief value, however, of this method is found in the estima-

tion of free chlorine existing in the so-called chloride of lime, chlorine water, hypochlorites of lime, soda, &c., in solution ; generally included under the term of chlorimetry.

1. Preparation of the Decinormal Solution of Sodid Arsenite.

4.95 gm. As_2O_3 per litre.

The iodine solution is the same as described in § 31, containing 12.7 gm. per litre.

The corresponding solution of sodid arsenite is prepared by dissolving 4.95 gm. of the purest sublimed arsenious anhydride free from sulphide, in about a $\frac{1}{4}$ litre of distilled water in a flask, with about 25 gm. of the purest crystallised sodid mono carbonate, free from sulphide, hyposulphite, or sulphite. It is necessary that the acid should be in powder, and the mixture needs boiling and shaking for some time in order to complete the solution ; when this is accomplished the mixture is diluted somewhat, then made up to the litre.

The equivalent number of arsenious acid being 198, and 1 atom absorbing 2 at. of oxygen, or liberating 4 of iodine, the $\frac{1}{40}$ part or 4.95 gm. is necessary to form the decinormal solution. 1 c.c. = 0.00495 gm. As_2O_3 .

In order to test this solution, 10 c.c. are put into a beaker with a little starch liquor, and the iodine solution allowed to flow in from a burette, graduated in $\frac{1}{10}$ c.c. until the blue colour appears, if exactly 10 c.c. are required the solution is strictly decinormal, if otherwise, the necessary factor must be found for converting it to that strength.

Starch liquor, however, cannot be used for the direct estimation of free chlorine, consequently resort must be had to an external indicator, and this is very conveniently found in iodide of starch paper, which is best prepared by mixing a portion of the starch liquor described in § 31. 3, with a few drops of solution of potassic iodide on a plate, and soaking strips of pure filtering paper therein ; the paper so prepared is used in the damp state, which is far more sensitive than the dried paper prepared according to Penot's plan.

2. The Analytical Process.

In all cases the chlorine to be estimated must exist in an alkaline solution. In the case of chloride of lime this is already accomplished by the caustic lime which invariably exists in the compound.

The substance being brought under the burette containing the

arsenious acid solution, it is suffered to flow until a drop of the mixture taken out with a glass rod and brought in contact with the prepared paper, no longer produces a blue spot. As the colour becomes gradually lighter towards the end of the process, it is not difficult to hit the exact point ; should it, however, by any accident be overstepped, starch liquor may be added to the mixture, and decinormal iodine solutions added until the blue colour is produced ; the quantity so used is then deducted from the total arsenic solution.

Examples : 50 c.c. of chlorine water were mixed with solution of sodic carbonate, and brought under the arsenic burette, and 20 c.c. of solution added ; on touching the prepared paper with the mixture no colour was produced, consequently the quantity used was too great ; starch liquor was therefore added and decinormal iodine, of which 3·2 c.c. were required to produce the blue colour. This gave 16·8 c.c. of arsenic solution, which multiplied by 0·00355, gave 0·05964 gm. Cl in the 50 c.c. A second operation with the same water required 16·8 c.c. of arsenic solution direct, before the end of the reaction with iodised starch paper was reached.

The arsenic solution is equally as serviceable as hyposulphite for the general estimation of iodine, sulphuretted hydrogen, chromates by distillation with hydrochloric acid, &c.

PART IV.

ANALYSIS BY PRECIPITATION.

INTRODUCTION.

§ 34. THE general principle of this method of determining the quantity of any given substance is alluded to in § 1, and in all instances is such that the body to be estimated forms an insoluble precipitate with a titrated reagent. The end of the reaction is, however, determinable in three ways.

1. By adding the reagent until no further precipitate occurs, as in the determination of chlorine by silver.

2. By adding the reagent in the presence of an indicator contained either in the liquid itself, or brought externally in contact with it, so that the slightest excess of the reagent shall produce a characteristic reaction with the indicator, as in the estimation of silver with salt, by the aid of potassic chromate, or that of phosphoric acid with uranium by yellow potassic prussiate.

3. By adding the reagent to a clear solution until a precipitate occurs, as in the estimation of cyanogen by silver.

The first of these endings can only be applied with great accuracy to silver and chlorine estimations. Very few precipitates have the peculiar quality of chloride of silver, namely, almost perfect insolubility, and the tendency to curdle closely by shaking, so as to leave the menstruum clear; some of the most insoluble precipitates, such as barytic sulphate and calcic oxalate, are unfortunately excluded from this class, because their finely-divided or powdery nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two substances, viz., the determination of cyanogen by silver, and that of chlorides by mercuric nitrate.

Since the estimation of chlorine or hydrochloric acid by precipitation with silver, can be used in many cases for the indirect estima-

tion of many other substances with great exactness, the preparation of the necessary standard solutions will now be described.

1. Preparation of the Decinormal Solution of Silver.

17 gm. AgNO_3 per litre.

10.8 gm. of pure silver are dissolved in pure nitric acid with gentle heat in a flask, into the neck of which a small funnel is dropped to prevent loss of liquid by spiriting; when solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to 1 litre; or if it be desired to use potassic chromate as indicator in any analysis, the solution must be neutral; in which case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in 1 litre; or, what is preferable, 17 gm. of pure and dry recrystallised nitrate of silver is dissolved in one litre of distilled water. If the grain system is used, 108 grn. silver or 170 grn. nitrate is dissolved, and the solution diluted to 10,000 grains.

1 c.c. of this solution = 0.0108 gm. Ag or
0.017 „ AgNO_3 .

2. Preparation of the Decinormal Solution of Salt.

5.85 gm. NaCl per litre.

5.85 gm. pure sodic chloride are dissolved in distilled water, and the solution made up to 1 litre, or 58.5 grn. to 10,000 grains.

There are two methods by which the analysis may be ended—

a. By adding silver cautiously, and well shaking after each addition till no further precipitate is produced.

b. By using a few drops of solution of potassic chromate as indicator, as devised by Mohr.

For the ending *a* refer to § 35. 1.

The ending *b* is exceedingly serviceable, on the score of saving both time and trouble. There are conditions, however, attached to its use, which must not be disregarded. The most important of these is, that the solutions must be absolutely free from acid or any great excess of alkali; it is best to have them neutral. When, therefore, acid is present in any solution to be examined, it should be neutralised with sodic carbonate in very slight excess.

CHLORINE.

$$\text{Cl.} = 35.5.$$

1 c.c. or 1 dm.	$\frac{N}{10}$	silver solution	= 0.00355 gm. or 0.0355 gm.
			Chlorine.
"	"	"	= 0.00585 gm. or 0.0585 gm.
			Sodic Chloride.

§ 35. THE powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the assay of silver by the wet method of Gay Lussac. The details of the process are more particularly described under the article relating to the assay of silver; the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic, and for exactness and convenient dilution are of decinormal strength. As just described, in many cases it is advisable to possess also centinormal solutions, made by diluting 100 c.c. $\frac{N}{10}$ solution to 1 litre.

1. The Analytical Process by Direct Precipitation.

Very weak solutions of chlorides, such as drinking waters, are not easily examined for chlorine by direct precipitation, unless they are considerably concentrated by evaporation previous to treatment, owing to the fact that, unless a tolerable quantity of chloride can be formed, it will not collect together and separate so as to leave the liquid clear enough to tell on the addition of fresh silver whether a distinct formation of chloride occurs. The best effects are produced when the mixture contains chlorine equal to from $1\frac{1}{2}$ to 2 gm. salt per 100 c.c. Should the proportion be much less than this, the difficulty of precipitation may be overcome by adding a quantity of freshly precipitated chloride, made by mixing equal volumes of $\frac{N}{10}$ salt and silver solution, shaking vigorously, pouring off the clear liquid, and adding the chloride to the mixture under titration. The best vessel to use for the trial is a well-stoppered round white bottle, holding 100 to 150 c.c., and fitting into a paper case, so as to prevent access of strong light during the analysis. Supposing, for instance, a neutral solution of potassic chloride requires titration, 20

or 30 c.c. are measured into the shaking bottle, a few drops of strong nitric acid added (free acid must always be present in direct precipitation), and a round number of c.c. of silver solution added from the burette. The bottle is placed in its case, or may be enveloped in a dark cloth and vigorously shaken for half a minute, then uncovered, and gently tapped upon a table or book, so as to start the chloride from the surface of the liquid where it often swims, downward; a quick clarification indicates excess of silver; the nearer the point of exact counterbalance the more difficult to obtain a clear solution by shaking, but a little practice soon accustoms the eye to distinguish the faintest precipitate.

In case of overstepping the balance in any trial, it is only necessary to add to the liquid under titration a definite volume of $\frac{N}{10}$ salt solution, and finish the titration in the same liquid—deducting, of course, the same number of c.c. of silver as have been added in salt solution.

Fuller details and precautions are given in the section on silver assay § 74. 3, to which the reader should refer.

2. The Analytical Process, with Potassic Chromate as indicator, specially applicable to Waters and Weak Solution of Chlorides.

To the neutral or faintly alkaline solution, four or five drops of a cold saturated solution of yellow potassic chromate is added, and the silver solution delivered from the burette until the last drop or two produce a permanent blood-red tinge, an evidence that all the chlorine has entered into combination with the silver, and the drop or two in excess has formed a precipitate of chromate of silver; the reaction is very delicate and easily distinguished.

Example: 1 gm. pure sodic chloride was dissolved in 100 c.c. of water, a few drops of chromate solution added, and titrated with $\frac{N}{10}$ silver, of which 17.1 c.c. were required to produce the red colour; multiplied by the $\frac{N}{10}$ factor for sodic chloride = 0.00585, the result was 1.00035 gm. NaCl, instead of 1 gm.

The determination of chlorides by Liebig's method, with mercuric nitrate, is described in § 80. 2.

INDIRECT ESTIMATION OF AMMONIA, SODA, POTASH, LIME, AND OTHER ALKALIES AND ALKALINE EARTHS, WITH THEIR CARBONATES, NITRATES, AND CHLORATES, ALSO NITROGEN, &c., BY MEANS OF DECINORMAL SILVER SOLUTION, AND POTASSIC BICHROMATE, AS INDICATOR.

1 c.c. $\frac{N}{10}$ silver solution = $\frac{1}{100000}$ atom of each substance.

§ 36. MOHR, with his characteristic ingenuity, has made use of the delicate reaction between chlorine and silver, with potassic chromate as indicator, for the determination of the bodies mentioned above. All compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid may be determined with great accuracy. The chlorine in a combined state is, of course, the only substance actually determined, but as the laws of chemical combination are exact and well known, the measure of chlorine is also the measure of the base with which it is combined.

a. In most cases it is necessary only to slightly supersaturate the alkali, or its carbonate, with pure hydrochloric acid; evaporate on the water bath to dryness, and heat for a time to 120° C. in the air bath, then dissolve to a given measure, and take a portion for titration.

b. Alkalies and Earths with organic acids are ignited to convert them into carbonates, then treated with hydrochloric acid, and evaporated as before.

c. Carbonic Acid in combination may be determined by precipitation with baric chloride, as in § 23, the washed precipitate is dissolved on the filter with hydrochloric acid, (covering it with a watch-glass to prevent loss,) then evaporated to dryness. In order to titrate with accuracy by the help of the potassic chromate, the baryta must be precipitated by means of a solution of pure sodic or potassic sulphate, added in slight excess; the precipitated barytic sulphate does not interfere with the delicacy of the reaction; if this precaution were not taken, the yellow barytic chromate would mislead.

d. Free Carbonic Acid is collected by means of ammonia and baric chloride, as in § 23, and the estimation completed as in c.

e. Chlorates are converted into chlorides by ignition, then titrated with $\frac{N}{10}$ silver and chromate.

f. Nitrates are evaporated with concentrated hydrochloric acid, and the resulting chlorides titrated as *e.*

g. Nitrogen. The ammonia evolved from guano, manures, oil-cakes, and sundry other substances, when burned with soda lime in Will and Varrentrapp's apparatus, is conducted through dilute hydrochloric acid; the liquid evaporated to dryness, and titrated as in *e.*

In all cases the operator will, of course, take care that no chlorine from extraneous sources but the hydrochloric acid is present, or if it exists in the bodies themselves as an impurity, its quantity must be first determined.

Example: 0.25 gm. pure sodic carbonate was dissolved in water, and hydrochloric acid added till in excess; then dried on the water-bath till no further vapours of acid were evolved; the resulting white mass was heated for a few minutes to about 120° C., dissolved and made up to 300 c.c.; 100 c.c. required 15.7 c.c. $\frac{N}{10}$ silver, this multiplied by 3 gave 47.1 c.c., which multiplied by the $\frac{N}{10}$ factor for sodic carbonate = 0.0053, gave 0.24963 gm. instead of 0.25 gm.

h. Indirect Estimation of Potash and Soda existing as Mixed Chlorides.

It is a problem of frequent occurrence to find the relative quantities of potash and soda existing in mixtures of the two alkalis—such as occur, for instance, in urine, manures, soils, waters, &c. The actual separation of potash from soda by means of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenient, since a careful estimation of the chlorine present in the mixture is the only labour required, and which can most readily be accomplished by $\frac{N}{10}$ silver and potassic chromate, as previously described.

1. The weight of the mixed pure chlorides is accurately found and noted.

2. The chlorides are then dissolved in water, and very carefully titrated with $\frac{N}{10}$ silver and chromate for the amount of chlorine present, which is also recorded; the calculation is then as follows:—

The weight of chlorine is multiplied by the factor 2.1029; from the product so obtained is deducted the weight of the mixed salts found in 1. The remainder multiplied by 0.36288 will give the weight of chloride of sodium present in the mixture.

The weight of sodic chloride deducted from the total as found in 1, will give the weight of potassic chloride.

$$\text{Sodic chloride} \quad \times 0.5302 = \text{Soda (NaO)}.$$

$$\text{Potassic chloride} \times 0.6317 = \text{Potash (KO)}.$$

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis. It is necessary, however, to bear in mind that this method of calculation can only be relied on when the two bases exist in about equal mixtures, or at least not less than $\frac{1}{3}$ of one to $\frac{2}{3}$ of the other.

PART V.

APPLICATION OF THE FOREGOING PRINCIPLES OF
ANALYSIS TO SPECIAL SUBSTANCES.

ALKALIES.

**TECHNICAL EXAMINATION OF COMMERCIAL
ALKALINE PRODUCTS.**

1. Soda Ash or Alkali.

§ 37. **MOISTURE** is determined by heating 5 or 10 gm. to dull redness for ten minutes, in a small crucible of platinum, silver, iron, or porcelain, allowing it to cool under a bell glass in the presence of sulphuric acid or calcic chloride; the difference between the first and second weighings is the accidental moisture in the sample.

The contents of the crucible are then dissolved in about 150 c.c. of warm distilled water, and any insoluble matter filtered off by a small filter, the latter washed a few times with hot water, then, if necessary, dried, ignited, and weighed as insoluble matter. It is important that this insoluble matter be removed before titration, otherwise the lime and other constituents in it will consume a portion of the normal acid, and so register a higher percentage of alkali than is really present.

The total quantity of alkali is determined in a measured portion of the filtrate and washing previously diluted up to $\frac{1}{2}$ or 1 litre, by normal sulphuric or oxalic acid, as in § 16.*

The quantity of caustic alkali present in any sample is determined as in § 16.

There prevails a custom in the soda trade of calculating the atomic weight of sodium as 24 instead of 23, thus representing more real soda present in a sample of alkali than actually exists; this practically leads to an error of from 1 to 2 per cent. in a 50 per cent. ash, according to the method of calculation. This anomaly ought to be got rid of, and one uniform standard adopted.

* This gives a slight error, owing to traces of aluminate of soda and lime, which consume acid.

The presence of sulphides is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated with an acid, or by dipping paper, steeped in sodic nitro-prusside, into the solution ; if the paper turns blue or violet, sulphide is present.

The quantity of sulphide and hyposulphite may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch liquor, and titrating with decinormal iodine solution (§ 31) till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and hyposulphurous acid present. The quantity of each may be known by adding a solution of sulphate of zinc to a like quantity of the alkali, and filtering so as to remove the free carbonated and sulphuretted alkali, by which means the hyposulphurous acid alone remains, which may be estimated with iodine and starch as before ; the quantity of iodine solution so required is to be deducted from the total, and the calculation for both sulphide and hyposulphite of sodium may then be made, 1 c.c. decinormal iodine is equal to 0.0248 gm. hyposulphite, or 0.0039 gm. sodic sulphide ; good English alkali is seldom contaminated with these substances to any extent.

Sodic chloride (common salt) may be determined by neutralising 0.585 gm. or 5.85 grn. of the alkali with nitric acid, and titrating with decinormal silver solution and potassic chromate (§ 36). Each c.c. or dm. corresponds to 1 per cent. of common salt, if the above weight is taken.

Sulphate of soda is determined, either direct or indirect, as in § 38 ; each c.c. or dm. of normal baric chloride is equal to 0.071 gm., or 0.71 grn. of dry sodic sulphate.

Black ash and raw mother liquors and lyes can be examined in precisely the same way as above ; if oxide of iron is present it may be determined as in § 28 ; lime, by boiling with sodic carbonate and precipitation as carbonate—washing the precipitate thoroughly with boiling water, and titration with normal acid and alkali, as in § 20. Phosphoric acid with uranium solution, as in § 71.

Mohr gives the following as a specimen of analysis of soda liquor volumetrically :—

(1.) Sp. gr. 1.252.

(2.) 10 c.c. evaporated to dryness left after slight ignition 3.11 grn. = 311 gm. per litre.

(3.) Residue of 2 titrated with normal nitric acid required 56.2 c.c. ; this includes the sodic sulphides.

(4.) 10 c.c. raw liquor neutralised with acetic acid required 6.82 c.c. $\frac{N}{10}$ iodine.

(5.) 10 c.c. precipitated with zinc sulphate to remove sulphide and the filtrate titrated with $\frac{N}{10}$ iodine required 2.44 c.c.

(6.) 10 c.c. raw liquor nearly neutralised with acetic acid and titrated for chlorine with $\frac{N}{10}$ silver and chromate required 11.4 c.c.

(7.) 10 c.c. raw liquor saturated with hydrochloric acid and titrated for sulphuric acid required 0.4 c.c. normal baric chloride.

The composition of the liquor was therefore as follows :—

(From 5.) The atomic weight of anhydrous sodic hyposulphite is 158 1 c.c. $\frac{N}{10}$ iodine = 0.0158—2.44 c.c. were required, therefore = 0.0385 gm. hypo.

(From 4.) The 2.44 c.c. iodine required in 5 deducted from the 6.82 c.c. in 4 leaves 4.38 c.c. to represent the sodic sulphide—1 c.c. $\frac{N}{10}$ iodine = 0.0039 gm. sulphide 4.38 c.c. = 0.017 gm.

(From 3.) The 4.38 c.c. iodine from 4 deducted from 56.2 c.c. normal acid leaves 55.76 c.c. which multiplied by the factor for sodic carbonate 0.053 gives 2.955 gm.

(From 6.) 11.4 c.c. $\frac{N}{10}$ silver $\times \frac{N}{10}$ factor for salt 0.00585 = 0.0669 gm.

Hence the results may be tabulated as follows :—

Sodic carbonate	2.9550 gm.
„ chloride	0.0669 „
„ sulphite	0.0284 „
„ hyposulphite	0.0385 „
„ sulphide	0.0170 „
	<hr/>
	3.1058
By evaporation	3.1100

In cases where an analysis of the total contents of a sample of black ash is required, the following method gives reliable results tolerably speedily. Most of the modes of determination are likewise applicable to samples of dry vat-waste :—(Wright*)

(a.) A known weight is dissolved in hydrochloric acid, the insoluble coke and sand collected on a weighed filter, and the carbon subsequently burnt off.

(b.) In the filtrate from (a) the H^2SO^4 is estimated by normal baric chloride.

(c.) A known weight is dissolved in nitric acid, and the Cl deter-

* Chem. News, vol. xvi. p. 151.

mined volumetrically by standard silver solution, or neutralised and titrated by the chromate method.

(*d.*) A known weight is titrated in Mohr's CO^2 apparatus fig. 20, the ammonium carbonate found precipitated by boiling with calcium chloride; the precipitate washed till the washings are neutral, dissolved in a slight excess of standard hydrochloric acid, and the excess determined by a standard alkaline solution; thus the CO^2 can be calculated.

(*e.*) A known weight is fused with four times its weight of a mixture of three parts dry sodium carbonate and one of potassium nitrate (both free from sulphate.) From the total sulphate thus formed, and estimated volumetrically by barium that existing as Na^2SO^4 is subtracted, and the remainder calculated as S.

(*f.*) A known weight is treated with hydrochloric acid, the filtrate oxidised by nitric acid, and the mixed Fe^2O^3 , Al^2O^3 and P^2O^5 precipitated by ammonia.

(*g.*) The filtrate from (*f.*) is treated with ammonic oxalate, the precipitate estimated volumetrically by permanganate, or gravimetrically as CaCO^3 ; hence the Ca is known.

(*h.*) A known weight is lixiviated with warm water, and in the filtrate from the insoluble matter the SiO^3 estimated by evaporation to dryness with hydrochloric acid; in the filtrate from this the Al^2O^4 combined as aluminate is determined by precipitating the alumina by ammonia.

(*i.*) A known weight is cautiously treated with sulphuric acid in a capacious platinum crucible, and heated till gases cease to be evolved; the residue is treated with water, filtered and well washed, ammonia and ammonium oxalate added to the filtrate; and ultimately the total Na contained weighed as Na^2SO^4 .

In calculating results from the foregoing data, the Cl found is calculated as NaCl, the SO^4 as Na^2SO^4 , the SiO^3 as Na^2SiO^3 , and the Al^2O^4 (soluble in water) as $\text{Na}^2\text{Al}^2\text{O}^4$; the remaining sodium is then calculated as Na^2CO^3 , and the remaining CO^3 as CaCO^3 . The sulphur is calculated as CaS, and the remaining calcium as CaO. From the total $\text{Al}^2\text{O}^3 + \text{Fe}^2\text{O}^3 + \text{P}^2\text{O}^5$ the alumina present as aluminate is subtracted; the coke and sand, &c., are directly terminated (*a.*) The difference from 100 in a carefully conducted analysis will not amount to more than a few tenths per cent, and represents cyanogen, traces of moisture, &c., and loss.

In an over-roasted ash the alkaline sulphide can only be safely estimated by digestion with nearly absolute alcohol, oxidation to

sulphate by chlorine, and precipitation by barium. The Na contained as poly, or mono-sulphide, may be determined volumetrically by test acid in the alcoholic solution, and must be subtracted from that to be calculated as Na^2CO^3 as above: the S existing as poly, or mono-sulphide of sodium must be subtracted from the total sulphur found, the difference being calculated as CaS. (For further information see Wright, Chem. Soc. Journ. XX. 407.)

2. Estimation of mixed Caustic Soda and Potash.

(Dale, Watt's Dict. vol. i. p. 119.)

This process depends upon the fact that potassic bitartrate is almost insoluble in a solution of sodic bitartrate.

Add to the solution containing the mixed salts, a standard solution of tartaric acid till neutral or faintly acid—this produces neutral tartrates of the alkalies—now add the same volume of standard tartaric acid as before—they are now acid tartrates, and the potassic bitartrate separates almost completely, filter off the sodic bitartrate and titrate the moist potassic bitartrate with normal caustic soda; the quantity required equals the soda originally in the mixture—the quantity of tartaric acid required to form bitartrate with the soda subtracted from the total quantity added to the mixture of the two alkalies, gives the quantity required to form potassic bitartrate, and thus the quantity of potash is found.

This process is only applicable for technical purposes, but nevertheless is very serviceable.

3. Potash and Pearlash

Are examined in the same way as soda.

4. Salt Cake

Is the impure sodic sulphate left in the retorts in preparing hydrochloric acid from sulphuric acid and salt, or nitric acid from sodic nitrate. It generally contains free sulphuric acid existing as sodic bisulphate, the quantity of which may be ascertained by direct titration with normal alkali.

The common salt present is estimated by decinormal silver solution and chromate; having first saturated the free acid with pure sodic carbonate, see § 36, 1 c.c. or 1 dm. silver solution; is equal to 0.00585 gm. or 0.0585 grn. of salt.

Sulphuric acid, combined with soda, is estimated either directly

or indirectly as in § 38; 1 c.c. or 1 dm. of normal baryta solution is equal to 0.071 gm., or 0.71 grn. of dry sodic sulphate.

5. Raw Salt, Brine, &c.

Lime may be estimated by precipitation with ammoniac oxalate, and the precipitate titrated with permanganate, as in § 57.

Sulphuric acid as in § 38.

Magnesia is precipitated as ammoniacal phosphate, by a solution of sodic phosphate containing ammonia, first removing the lime by ammoniac oxalate, the precipitate of double phosphate of magnesia and ammonia is brought on a filter, washed with cold water containing ammonia, then dissolved in acetic acid, and titrated with uranium solution, as in § 71; each c.c. of solution required represents 0.0563 gm. magnesia; or the precipitate may be dried, ignited, and weighed as magnesian pyrophosphate.

The quantity of real salt in the sample may be ascertained by treating a weighed quantity in solution with caustic baryta, boiling, setting aside that the excess of baryta may precipitate itself as carbonate, or more quickly by adding ammoniac carbonate, filtering, evaporating the solution to dryness, and gently igniting—the residue is pure salt. The loss of weight between this and the original specimen taken for analysis, will show the percentage of impurities.

6. Gypsum, Selenite, Plaster of Paris

May be estimated direct by boiling a weighed quantity, in fine powder, with its own weight of sodic carbonate, and about 20 parts water for half-an-hour, adding fresh water to supply the waste; the calcic carbonate so formed is brought upon a filter, washed thoroughly with boiling water, and the precipitate and filter titrated with normal acid and alkali, as in § 14. 5.

Sulphuric acid may be estimated in the filtrate from above, directly or indirectly, by normal baric chloride, as in § 38.

The indirect estimation of gypsum is obtained by boiling 3 gm. with 60 c.c. of normal sodic carbonate for some time in a 300 c.c. flask, dilute to the 300 c.c. mark, and put aside to settle, take out 100 c.c. of the clear liquid with a pipette, and titrate with normal acid and alkali, multiply the quantity of acid by 3, and deduct the product from the original 60 c.c. of alkali. The remainder is calculated as hydrated calcic sulphate, by multiplying with 0.086, or as anhydrous with 0.068.

7. Ammonical Gas Liquor.

The value of this substance depends upon the quantity of ammonia contained therein; this constituent mainly exists in a free state, some portion of it, however, generally exists as sulphide and hyposulphite of ammonium. The free alkali is best determined by titrating a known volume of the liquor with normal acid and litmus; in consequence of the dark colour and other contaminations of the liquor, it is more secure to ascertain the end of the process by litmus paper—a glass rod or small feather moistened with the mixture may be brought in contact with both red and blue paper, when both remain unaffected the process is finished; each c.c. or dm. of acid is equal to 0·017 gm., or 0·17 grn. of ammonia.

The total quantity of ammonia is ascertained by distilling a portion of the gas liquor in the apparatus, fig. 11. Or an equally exact process, when the liquor contains no other salt than ammonia, consists in saturating a portion of the liquor with pure hydrochloric acid, and evaporating to perfect dryness on the water-bath, then heating the residue to about 120° C. in the sand or air-bath, dissolving in water, filtering and titrating with decinormal silver solution and chromate, as in § 36.

Each c.c. or dm. of $\frac{N}{10}$ silver solution, is equal to 0·0017 gm. or 0·017 grn. of ammonia.

Hydrosulphuric and hyposulphuric acids can be estimated with $\frac{N}{10}$ iodine solution, as in the case of alkali. (§ 37.1.)

8. Soap.

The only volumetric method that appears worth anything in the examination of commercial soaps, is based upon the principle of Clark's soap test for estimating the hardness of water. A standard soap is first chosen by means of which the relative saponifying power of any other soap may be ascertained.

Mottled Marseilles soap, generally known as Castile soap, may be taken as such a standard. This soap contains 30 per cent. of water, and is free from all mineral adulteration; its composition is, in round numbers,

Soda	6
Fatty acids	64
Water	30
	<hr/>
	100

1 gm. of this soap will be exactly neutralised by 0·1074 gm. pure calcic chloride, or 10 grains by 1·074 gm.

Therefore a solution of 1·074 gm. CaCl^2 in a litre of water or 10·74 grn. in 1000 dm. will suffice to neutralise respectively 10 gm. or 100 grn. of standard soap dissolved in the same volume of water, or rather alcohol and water.

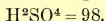
The smallest excess of soap solution will give the persistent froth as in Clark's test.

Pons (*Journ. de Ph. et Chem. Ap.* 1865, p. 290,) applies the process as follows :—10 c.c. of the standard calcic solution are placed in a stoppered bottle holding 70—100 c.c. with about 20 c.c. distilled water; 10 gm. soap is then dissolved in 100 c.c. alcohol, '825 sp. gr., by means of rubbing or shaking with gentle heat—the real soap dissolves and leaves all mineral or foreign matters, which may be filtered off, and afterwards examined if necessary; the filtered soap solution is now diluted to one litre with distilled water, and a burette filled with it ready to add to the lime solution in the shaking bottles. It is then cautiously run into the lime with frequent shaking until a lather is obtained; the 10 c.c. of lime solution divided by the number of c.c. of soap solution required, will show the richness of the soap as compared with the standard—if 10 c.c. only is used, the soap under examination is of the same quality as the standard; if 15 or 20 c.c. are required, the percentage will be $\frac{10}{15} = 66\%$ or $\frac{10}{20} = 50\%$, and so on.

The alkali may be determined by igniting a weighed quantity of the dry soap, and titrating with normal acid—if salt is present it may be estimated in the ash by $\frac{N}{10}$ silver and chromate. (§ 36.)

SULPHURIC ACID AND SULPHATES

Monohydrated Sulphuric Acid.



Sulphuric Anhydride.



1. Mohr's Method.

§ 38. THE indirect process devised by C. Mohr, and fully described in the "*Annalen der Chemie und Pharmacie*," Bd. 90, S. 165, depends upon the same method of determination as has already been described for the alkaline earths, that is to say, a known volume

of baryta solution is added to the compound, more than sufficient to precipitate the sulphuric acid, the excess of baryta is converted into carbonate, and titrated with normal acid and alkali, as described in § 23.

It is best to use a normal solution of baric chloride as the precipitant, which is made by dissolving 122·05 gm. of pure chloride in the litre ; this solution likewise suffices for the determination of sulphuric acid by the direct method.

The following is the method of procedure.

If the substance contains a considerable quantity of free acid, it must be brought near to neutrality by pure sodic carbonate ; if alkaline, to be slightly acidified with hydrochloric acid, a round number of c.c. of baryta solution is then added, and the whole digested in a warm place for some minutes ; then precipitate the excess of baryta by a mixture of carbonate and caustic ammonia in slight excess ; if a little piece of litmus paper be thrown into the mixture, a great excess can readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, and thoroughly washed with boiling water, then titrated as in § 23.

The difference between the number of c.c. of baryta solution added, and those of normal acid required for the carbonate, will be the measure of the sulphuric acid present ; each c.c. of baryta solution is equal to 0·040 gm. SO^3 .

Example : 2 gm. pure and dry barytic nitrate, and 1 gm. pure potassic sulphate were dissolved, mixed, and precipitated hot with carbonate and caustic ammonia ; the precipitate, after being thoroughly washed, gave 1·002 gm. potassic sulphate, instead of 1 gm.

For technical purposes this process may be considerably shortened by the following modification, which dispenses with the washing of precipitate.

The solution containing the sulphates or sulphuric acid is first rendered neutral—normal baric chloride is then added in excess, then normal sodic carbonate in excess of the baric chloride, and the volume of both solutions noted ; the liquid is then made up to 200 or 300 c.c. in a flask, and an aliquot portion filtered off and titrated with normal acid, the difference between the baric chloride and sodic carbonate gives the sulphuric acid.

The solution must of course contain no substance precipitable by sodic carbonate except the baryta (or if so, previously removed), nor must it contain any substance precipitable by baryta, such as phosphoric or oxalic acid, &c.

2. Titration by Baric Chloride, with Potassic Chromate as indicator (Wildenstein.)

In Fresenius' "Zeitschrift für Analytische Chemie," part 3, Wildenstein has announced a method for the more rapid and secure estimation of sulphuric acid, the principle of which is as follows :—

To the hot and somewhat concentrated sulphuric acid solution, (which must be neutral, or if acid, neutralized with caustic ammonia, free from carbonate,) a standard solution of baric chloride is added in slight excess, then a solution of potassic chromate, of known strength, is cautiously added to precipitate the excess of baryta ; so long as any baryta remains in excess, the supernatant liquid is colourless, when it is all precipitated the liquid is yellow, from the free chromate ; as a few drops only of a solution of chromate are necessary to produce a distinct colour, the process is capable of very good results.

The standard solution of baric chloride may be normal, that is, 122.05 gm. per litre, 1 c.c. = 0.040 gm. SO^3 . The potassic chromate also normal = 97.35 gm. per litre, 1 c.c. = 0.040 gm. SO^3 , or 0.122 gm. Ba Cl^2 .

The use of solutions of this strength, however, necessitates great care in the analytical process, lest the end of reaction should be overstepped too hastily, but it has the convenience of requiring little calculation.

Wildenstein uses a baryta solution, of which 1 c.c. = 0.015 gm. SO^3 , and chromate of potash 1 c.c. = 0.010 gm. SO^3 . It would, I think, be preferable to use seminormal solutions, so that 1 c.c. of each would be equal to 0.020 gm. SO^3 . If the chromate solution is made to possess the same chemical power as that of the chloride, the operator has simply to deduct the one from the other in analysis, in order to obtain the quantity of baryta really required to precipitate all the sulphuric acid.

The analytical process.—The substance or solution containing sulphuric acid is brought into a small wide-mouthed flask, diluted to about 50 c.c., if acid, neutralized with pure ammonia in slight excess, heated to boiling, and the baric chloride delivered cautiously from the burette, till in slight excess ; as the precipitate rapidly settles from a boiling solution, it is not difficult to avoid great excess of baryta, which would prevent the liquid from clearing so speedily.

The flask is then put over the lamp again, heated to boiling, and the chromate solution added in $\frac{1}{2}$ c.c. or so, each time removing the flask from the lamp, and allowing to settle until the supernatant liquid is of a light yellow colour ; the quantity of chromate solution is then deducted from the baryta, and the remainder calculated for SO^3 .

Or the mixture with baryta in excess may be diluted to 100 or 150 c.c., the precipitate allowed to settle thoroughly, and 25 or 50 c.c. of the clear liquid taken out, heated to boiling, and precipitated with chromate until all the baryta is carried down as barytic chromate, leaving the supernatant liquid of light yellow colour ; if there is any uncertainty in the first titration, the analysis may be checked by a second.

3. Direct Precipitation with Normal Baric Chloride.

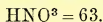
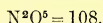
Very good results may be obtained by this method when carefully performed. The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the baryta solution allowed to flow cautiously in from the burette until no further precipitation



Fig. 25.

occurs. The end of the process can only be determined by filtering a portion of the liquid, and testing with a drop of the baryta solution. Dr Beale's filtering tube, shown in fig. 25, is the best aid in this case ; a piece of fine filtering paper is tied over the lower end, which is then to be dipped about half an inch into the liquid, which rises into the tube perfectly clear ; a little is to be poured into a test tube and a drop of baryta added from the burette ; if a cloudiness occurs, the contents of the tubes must be emptied back again, washed out into the liquid, and more baryta added until all the sulphuric acid is precipitated ; a decinormal solution of baryta is advisable towards the end of the process.

Instead of the test tube for ascertaining whether baryta or sulphuric acid is in excess, a plate of black glass, or a sheet of white glass upon black paper may be used, upon which a drop of the clear solution is placed and tested by either a drop of baric chloride or sodic sulphate,—these testing solutions are preferably kept in two small bottles with elongated stoppers.

NITRIC ACID AND NITRATES.**Hydrated Nitric Acid.****Nitric Anhydride.****Factors.**

Normal acid	×	0.063 = HNO^3
Ditto	×	0.054 = N^2O^5
Ditto	×	0.101 = KNO^3
Metallic iron	×	0.375 = HNO^3
Ditto	×	0.6018 = KNO^3

§ 39. THE accurate estimation of nitric acid in combination presents great difficulties, and can only be secured by indirect means ; the methods here given are sufficient for most purposes ; very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

1. Gay Lussac's method modified by Abel (applicable only to Alkaline Nitrates.)

This process depends upon the conversion of nitrates of soda or potash into carbonates by ignition with carbon, and the titration of the carbonate so obtained, by normal acid, as described in alkali-metry. The number of c.c. of normal acid required multiplied by 0.101, will give the weight of pure potassic nitrate in grammes ; by 0.085, the weight of sodic nitrate in grammes.

The best method of procedure is as follows :—The sample is finely powdered and dried in an air bath, and 1 gramme, or an equivalent quantity in grains, weighed, introduced into a platinum crucible, and mixed with a fourth of its weight of pure graphite, (prepared by Brodie's process,) and four times its weight of pure ignited sodic chloride. The crucible is then covered and heated moderately for twenty minutes over a Bunsen's burner, or for eight or ten minutes in a muffle (the heat must not be so great as to volatilise the chloride of sodium to any extent.) If sulphates are present they will be reduced to sulphides ; and as these would

consume the normal acid, and so lead to false results, it is necessary to sprinkle the fused mass with a little powdered potassic chlorate, and heat again moderately till all effervescence has ceased. The crucible is then set aside to cool, warm water added, the contents brought upon a filter, and washed with hot water till the washings are no longer alkaline. The filtrate is then titrated with litmus and normal acid in the ordinary way, or better by the residual method described in alkalimetry.

2. Acidimetric Method.

The principle of this mode of determining nitric acid is described in § 24, but is only applicable where the base is precipitable by pure or carbonated alkalies, and where no other acid is present, having a precipitable base; with nitrates of metallic oxides and alkaline earths, very accurate results are obtained.

3. Estimation of Nitrates by Distillation with Sulphuric Acid.

This method is of very general application, but particularly so with the impure alkaline nitrates of commerce; the process, however, needs careful manipulation, but yields accurate results.

There are two methods of procedure.

a. To bring the weighed nitrate into a small tubulated retort with a cooled mixture of water and strong sulphuric acid, in the proportion of 10 c.c. water and 5 c.c. sulphuric acid for 1 gm. of nitrate; the neck of the retort is drawn out to a point and bent downward, entering a potash or other convenient bulb apparatus containing normal caustic alkali; the retort is then buried to its neck in the sand-bath, and heated to 170°C. , (338°Fahr.) so long as any liquid distils over; the heat must never exceed 175°C. (347°Fahr.) otherwise traces of sulphuric acid will come over with the nitric acid. The quantity of acid distilled over is found by titrating the fluid in the receiver with normal acid as usual.

b. Distillation in a Partial Vacuum, (Finkener.) By this arrangement there is no danger of contaminating the distillate with sulphuric acid, inasmuch as the operation is conducted in a water bath, and when once set going needs no superintendence.

The retort is the same as before described, but the neck is not drawn out or bent; the stopper of the tubulure must be well ground. The receiver is a 200 c.c. flask with narrow neck, containing the requisite quantity of normal alkali diluted to about 30 c.c.

The receiver is bound, air tight, with the neck of the retort, (which should reach nearly to the middle of the flask,) by means of a vulcanized tube: the proportions of acid and water before mentioned are brought into the retort with a tube funnel. The stopper of the retort is then removed, and the contents, both of the receiver and retort, heated by spirit or gas lamps to boiling, so as to drive out the air; the weighed nitrate contained in a small tube is then dropped into the retort, the stopper inserted, the lamps removed, and the retort brought into the water bath, while the receiver is kept cool with wet tow or placed in cold water. The distillate is titrated as before; 1 or 2 gm. saltpetre, require about four hours for the completion of the process. According to H. Rose, (*Zeitschrift für an Chem.* Part iii., page 311,) Finkener obtained very accurate results by this method.

When chlorides are present in the nitrate a small quantity of moist oxide of silver is added to the mixture before distillation.

4. Estimation by conversion into Ammonia (Schulze and Vernon Harcourt).

The principle of this method, which gives very satisfactory results, is based on the fact that when a nitrate is heated with a strong alkaline solution and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Schulze found that when the zinc was platinised, or when sodium or aluminium amalgam was used, the reaction was perfect.—(*Chem. Centr. blatt*, 1861, pp, 657 and 833.) Vernon Harcourt appears to have arrived independently at the same result, by using a mixture of iron and zinc.—(*Journal of Chem. Soc.*, 1862, p. 381).

As the latter process seems, on many accounts, preferable to that of Schulze, a short description of the apparatus, etc., devised by Harcourt is given.

The distilling flask holds about 200 c.c., and is closely connected, by a bent tube, with another smaller flask in such a manner that both may be placed obliquely upon a sand bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spirting of the boiling liquids from entering the exit tubes, but as a further precaution, these latter are in both flasks turned into the form of a hook; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser, (which may be made of wide glass tube), into

an ordinary tubulated receiver, containing normal sulphuric acid coloured with litmus, the end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid ; instead of this latter, however, a chloride of calcium tube, filled with broken glass and moistened with acid, will answer the purpose ; the distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a good fitting vulcanised tube ; by this means water may be passed through the tube when the distillation is over, so as to remove any traces of ammonia which may be retained on its sides ; all the corks of the apparatus should be soaked in hot paraffin so as to fill up the pores.

All being ready, about 50 gm. of finely granulated zinc* (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) is put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible ; the weighed nitrate is then introduced, either in solution or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sand-bath heated by a gas-burner, a little water is previously put into the second flask. Convenient proportions of material are $\frac{1}{2}$ gm. nitre and about 20 c.c. each of water, and solutions of potash spec. grav. 1.3.

Heat is now applied to that part of the sand-bath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point ; when distillation has actually commenced, the water in the second flask is made to boil gently ; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may escape the first, are sure to be retained in the second flask. The distillation with the quantities above named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass ; the contents of the receiver are then titrated with normal caustic potash or soda as usual.

Chlorides and sulphates do not interfere with the accuracy of the results.

* After the distillation is over, the zinc and iron may be well washed, then dried, and preserved for the next operation.

A mean of several experiments with pure nitre gave 53.3 % of nitric acid instead of 53.41 %. The process does not give such accurate results with some metallic nitrates.

Siewert has suggested a modification of this process—the distilling apparatus is a 300–350 c.c. flask with tube leading to two small flasks connected together as wash bottles, and containing standard acid. For 1 gm. nitre, 4 gm. iron, and 10 gm. zinc filings, with 16 gm. caustic potash and 100 c.c. alcohol .825, are necessary ; after digesting for half an hour in the cold or in slight warmth, a stronger heat may be applied to drive out all the ammonia into the acid flasks—finally 10–15 c.c. fresh alcohol is admitted to the distilling flask and distilled off to drive over the last traces of ammonia, and the acid solution then titrated residually as usual.

Chapman recommends the nitrate to be digested in cold solution containing a considerable quantity of caustic potash, with an unweighed excess of aluminium in thin sheet or filings ; after the conversion is complete (say during a night), the ammonia is distilled off into standard acid and estimated residually ; the apparatus, fig. 19, answers very well for this purpose.

5. Pelouze's Method.

The principle upon which this well-known process is based is as follows :

a. When nitrate is brought in contact with a solution of ferrous oxide, mixed with free hydrochloric acid, and heated, part of the oxygen contained in the nitric acid passes over to the iron, forming a persalt, while the base combines with hydrochloric acid, and nitric oxide (NO^2) is set free ; 3 atoms of iron = 168 are oxidised by 1 at. nitric acid = 63. If, therefore, a weighed quantity of the nitrate be mixed with an acid solution of ferrous chloride or sulphate, of known strength, in excess, and the solution boiled, to expel the liberated nitric oxide, then the amount of unoxidised iron remaining in the mixture, found by a suitable method of titration, the quantity of iron converted from ferrous into ferric oxide, will be the measure of the original nitric acid in the proportion of 168 to 63, or by dividing 63 by 168, the factor 0.375 is obtained, so that if the amount of iron changed as described be multiplied by this factor, the product will be the amount of nitric acid.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of

ferrous oxide absorbs oxygen from the atmosphere. On this account accurate results are only obtained by conducting hydrogen or carbonic acid gas through the apparatus while the boiling is carried on. This modification has been adopted by Fresenius with very satisfactory results. The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward, a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through while it is being dissolved; the solution so obtained, or one of double sulphate of iron and ammonia of known strength being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for ten minutes or so, then boiled until the dark red colour of the liquid disappears, and gives place to the brownish yellow of ferric chloride; the retort is then suffered to cool, the circulation of carbonic acid or hydrogen still being kept up, then the liquid diluted freely and titrated with permanganate $\frac{N}{10}$, as in § 27. Owing to the irregularities attending the use of permanganate with hydrochloric acid, it may be preferable to dilute the solution less, and titrate with bichromate, as in § 30. 2 gm. pure iron, or its equivalent in double iron salt, $\frac{1}{2}$ gm. saltpetre and about 60 c.c. strong hydrochloric acid, are convenient proportions for the analysis.

b. Direct titration of the resulting ferric chloride. This modification of Pelouze's original method was suggested by Braun, (*Journ. f. pract. Chem.*, 81, 421), and is decidedly better in principle than the residual titration of the ferrous chloride by permanganate. Braun, however, estimates the peroxide by adding an excess of potassic iodide, digesting for a time at a gentle heat, then titrating the resulting free iodine by sodic hyposulphite. 3 eq. of iodine so found corresponding to 1 eq. nitric acid; the disadvantage possessed by this plan is that variable quantities of water, or hydrochloric acid, seriously affected the accuracy of the results. Fresenius has therefore suggested the use of stannous chloride for titrating the ferric oxide, with the best results (*Zeitschrift f. an. Chem.*, part 1, p. 34).

The following plan of procedure is recommended as the best by the same authority.

A solution of ferrous sulphate is prepared by dissolving 100 gm.

of the crystals in 500 c.c. of hydrochloric acid of spec. grav. 1.10; when used for the analysis, the small proportion of peroxide of iron invariably present in it is found by titrating with stannous chloride, as in § 41. The nitrate being weighed or measured, as the case may be, is brought together with 50 c.c. (more or less, according to the quantity of nitrate) of the iron solution into a long necked flask, through the cork of which two glass tubes are passed, one connected with a carbonic acid apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The carbonic acid tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for ferric chloride, as in § 41. The liquid must, however, be suffered to cool before titrating with iodine for the excess of stannous chloride. While cooling, the stream of carbonic acid should still be continued. The quantity of iron changed into peroxide, multiplied by the factor 0.375, will give the amount of nitric acid. Example :

a. A solution of stannous chloride was used for titrating 10 c.c. of solution of pure ferric chloride, containing 0.215075 gm. iron. 25.65 c.c. of tin solution were required, therefore that quantity was equal to 0.0807 gm. HNO_3 , or 0.069131 gm. N^2O^5 .

b. 50 c.c. of acid ferrous sulphate were titrated with tin solution for ferric oxide, and 0.24 c.c. were required.

c. 1 c.c. tin solution = 3.3 c.c. iodine solution.

d. 0.2177 gm. of pure nitre was boiled, as described, with 50 c.c. of the acid ferrous sulphate, and required respectively 45.03 c.c. tin solution, and 4.7 c.c. iodine—

$$4.7 \text{ iodine solution} = 1.42 \text{ Sn. Cl}^2.$$

$$\text{The peroxide in the protosulphate solution} = 0.24 \text{ „}$$

$$1.66$$

$45.03 - 1.66 = 43.37$, therefore $25.65 : 0.069131 = 43.37 : x$, = 0.1169 N^2O^5 instead of 0.1163, or 53.69% instead of 53.41. A mean of this, with three other estimations, using variable proportions of tin and iron solutions, gave exactly 53.41%. The process is therefore, though troublesome, entirely satisfactory.

6. Direct Titration of the resulting Ferric Chloride by Iodine and Hyposulphite.

Mohr proceeds as follows:—The dry nitrate with 12 times its weight of double iron salt is placed in a 100—150 c.c. flask, with about 50 c.c. hydrochloric acid and a little water. The flask is closed with a cork through which is passed a glass tube cut slantwise below the cork; about $1\frac{1}{2}$ inch of stout vulcanised tube is then fixed over the upper end of the glass tube and closed with a piece of solid glass rod—a slit is cut vertically in the elastic tube so that when the contents of the flask boil the steam may escape from the valve so formed—the atmospheric pressure closes this valve when boiling ceases—the contents are boiled till all the nitric oxide is driven off and the solution is the colour of ferric chloride, then cooled, and a sufficiency of potassic iodide added to decompose the ferric chloride; when this is complete, starch is added and the mixture titrated with hyposulphite; as the oxygen in nitric acid represents three times its equivalent of hyposulphite,

$$\frac{0.0063}{3} = 0.0021 \text{ HNO}^3 \text{ or } \frac{0.0101}{3} = 0.00337 \text{ KNO}^3—$$

the quantity of hyposulphite used multiplied with either of these factors will give the quantity of nitric acid or potassic nitrate. Mohr obtained by this method very reliable results.

P. Holland has suggested an admirable modification of apparatus for estimating nitric acid by Pelouze's process, (*Chem. News*, vol. xvii. p. 219). The operation is conducted in vacuo, and the necessity of using an atmosphere of hydrogen or carbonic acid is entirely obviated; the apparatus is simple and easily arranged, and appears to have yielded to the author very satisfactory results. A sketch of the apparatus is given in the article referred to.

7. Schlösing's Method.

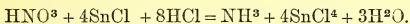
The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of ferrous chloride drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime; the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with normal alkali as usual.

This method was devised by Schlösing for the estimation of nitric acid in tobacco, and is especially suitable for that and similar

purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0.15 gm., the process is very accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found either in the author's original paper, "*Annal. de Chim.*," 3 sér., tom. 40, 479, or "*Journ. für pract. Chem.*," 62, 142, also abridged in "*Fresenius' Quantitative Analysis*," fourth German, or second English edition. The process is less troublesome in practice than is generally supposed.

8. Estimation by conversion into Ammonia with Stannous Chloride, (Pugh.)

This process is based on the fact that when a nitrate is digested under pressure, and at a temperature of about 160° C. with an excess of stannous chloride and hydrochloric acid, the following reaction occurs:—



1 eq. of nitric acid, therefore, under the above conditions, converts 4 eq. of tin from the state of proto to perchloride, consequently, if an unknown quantity of nitric acid be digested with a sufficient excess of stannous chloride of known strength, and the quantity changed into perchloride be afterward found by a suitable method of titration, the proportion of nitric acid will be found, supposing in all cases that no other substance is present, capable of affecting the same change in the tin solution.

Pugh arrived at the knowledge of the reaction described, by careful experiments, which are detailed in the *Quarterly Journal of the Chemical Society*, (vol. xii., part 1, page 35,) and used the process devised by Streng for titrating the strength of the tin solution, namely, potassic bichromate, potassic iodide, and starch. Experience has shown, however, that the estimation of tin by this method is far from satisfactory, owing to the variable amount of oxidation which the tin solution undergoes when different quantities of water or acid are present during the titration.

In my experiments on the process, I have therefore adopted the method of Lenssen (§ 54. 1) for estimating the strength of the tin solution, with the most satisfactory results, using in all cases an accurately weighed quantity of pure potassic nitrate for the analysis. One example in detail will make the process clear.

a. A solution of pure nitre was prepared so that 1 c.c. = 0.1 gm. KNO_3 .

b. A solution of pure tin in hydrochloric acid, as in § 30.3.

c. A piece of stout combustion tube, about half an inch diameter and fifteen inches long, was closed at one end, then heated before the blowpipe at about nine inches from the closed end, and drawn out for the space of an inch to a narrow neck; the tube was then cut off just above this neck, so as to leave a kind of funnel mouth.

d. 1 c.c. of the tin solution was measured with a very accurate pipette into a good sized flask; about 3 or 4 c.c. of saturated solution of Rochelle salt added; then a solution of pure sodic carbonate, till all effervescence was over, and the liquid clear and slightly alkaline; the sides of the flask were then washed down with cold distilled water, and about 20 c.c. of saturated solution of sodic bicarbonate delivered in; then starch liquor, and $\frac{N}{10}$ iodine solution from a $\frac{1}{10}$ c.c. burette, till the blue colour appeared. 17.9 c.c. were required, and as 1 c.c. of $\frac{N}{10}$ iodine corresponds to 0.0059 tin, 1 c.c. of the tin solution contained 0.10561 gm. tin.

e. 2 c.c. of the solution *a* were then measured into the tube *c*. 14 c.c. of tin solution added, the funnel neck washed down with a few drops of water, a fragment of pure marble dropped in to produce carbonic acid, and thus dispel all air from the tube; when the evolution of gas had ceased, the neck was heated and well closed; about two inches of space was thus left filled with carbonic acid. When the closed end was cooled, the tube was shaken so as to mix the liquids well, put into a copper air bath, and heated up to 160°C . for about fifteen minutes; then allowed to cool, and when perfectly cold the end of the tube broken off, the contents transferred to a large flask, and treated with the alkaline tartrate and carbonate, as in *d*; the tube was then washed through with cold distilled water into the flask, sodic bicarbonate, in solution or in powder added, and the unchanged tin solution titrated with $\frac{N}{10}$ iodine, as described in *d*, the quantity required was 88.6 c.c. The calculation was therefore as follows.

1 c.c. tin solution = 0.10561 gm. tin, consequently 14 c.c. = 1.47854 gm., from this must be deducted the weight of tin corresponding to 88.6 c.c. $\frac{N}{10}$ iodine = 0.52274 gm., showing that 0.9558 gm. of tin had been changed by the nitric acid present; this in turn being multiplied by the factor 0.1144, (obtained by dividing the atomic weight of nitric acid by four times the eq. of tin,) gave 0.10934 gm. N^2O_5 , theory requires that 0.2 gm. K,NO_3 should

contain 0.10693 gm. In this case, therefore, the percentage of nitric acid in the salt was found to be 54.67, whereas it should be 53.41; but the mean of fifteen experiments made with variable quantities both of tin solution and nitrate, (always taking care that at least 10 eq. of tin were present for every one eq. of nitric acid,) gave 54.1% instead of 53.41.

The titration with iodine may be entirely dispensed with by distilling the ammonia from the tin solution after digestion, in the apparatus shown in fig. 19; in this case the liquid is simply neutralised with caustic soda or potash, brought into the distilling flask, an excess of caustic alkali added, the contents of the flask boiled, as in § 17, the ammonia received into normal acid, and titrated in the ordinary way.

Chapman and Schenk have found that in estimating nitrates in substances containing nitrogenous organic matter, such as sewage or other impure waters, Pugh's process is not reliable. Albumen, gelatine, or urea, evolve ammonia by digestion with stannous chloride without the latter being the least oxidised in the process.

In the case of water residues or other matters containing organic matter of a non-nitrogenous character, the nitric acid must not be estimated by the oxidation of the stannous salt, but by distillation of the ammonia.

When no organic matters affecting the tin solution are present, the process is very reliable. Gallic and pyrogallic acids or mannite have no reducing effect on the tin.

If sulphuric acid or a soluble sulphate is present in the substance digested with the solution of tin, sulphurous acid will be formed; baric sulphate is, however, not affected, consequently it is necessary to precipitate the sulphuric acid by baric chloride, previous to digestion, when the method of estimation by iodine is used.

Crum's excellent method for the estimation of nitric acid as adopted by Frankland and Armstrong in the analysis of water residues, is fully described in the section on Water analysis, Part 6.

9. Estimation by Indigo Solution.

Marx (Fresenius' Zeitschrift, vol. vii., p. 412) has devised a process for the estimation of nitrates and nitrites in potable waters which occupies little time, but which cannot be depended upon for absolute accuracy—it may however be adopted for an approximate estimation where the water does not contain more than 5–6 milligrammes of nitric acid in 50 c.c., or about 0.1 gm. per litre.

A standard solution of potassic nitrate is first prepared, which may conveniently contain 2.0258 gm. per litre—1 c.c. will then equal 0.00101 gm. KNO_3 or 0.00063 HNO_3 ; this solution is used for ascertaining the strength of the indigo, which is simply a dilute solution of indigo in sulphuric acid.

The titration is as follows :—5 c.c. of nitrate solution is put into a flask with 45 c.c. of distilled water, and 100 c.c. of pure strongest sulphuric acid added—the mixture rises to the temperature of about 120°C .—the indigo is now added from a burette until it ceases to lose its colour, and the final drop tinges the mixture bluish green. From this experiment the strength of the indigo is found and noted.

The temperature of the liquid must not be allowed to fall below 100°C .

In examining waters—50 c.c. of the sample is put into a 250 c.c. flask, 100 c.c. sulphuric acid added, and titrated with indigo, as just described—the strength of the indigo solution being known from the titration with standard nitrate solution, the calculation can readily be made for the water.

Chlorides being present has no effect on the result. The end of the process is difficult to distinguish if the proportion of nitric acid present is larger than mentioned above.

10. Estimation of Ammonia and Nitrates by Conversion into Nitrogen Gas, with Bromised Sodid Hypochlorite.

Krocker and Dietrich have experimented upon this method originally devised by Knop, but instead of measuring the volume of nitrogen gas produced, which does not always give exact results, they use an excess of the oxidising agent, and after the action is complete—estimate the excess residually with $\frac{N}{10}$ arsenious solution and iodised starch paper, as in § 33 (Fresenius' Zeitschrift für an. Chem. iii., 64) in the case of pure ammoniacal salts or nitrates the results are extremely satisfactory, and also with other compounds where there is nothing present to affect the bromised solution.

a. Preparation of the Chloro-bromous Solution.

1 part of crystals of sodic carbonate is dissolved in 15 parts of cold distilled water, and chlorine gas passed through the solution till completely saturated; to the fluid is then added a sufficiency of 25 per cent. caustic soda solution to render the whole slippery when rubbed between the fingers. Bromine is then added to the mixture

until a distinct lemon colour is produced. The addition of the bromine is, however, always preferably made just before the solution has to be used for a series of experiments.

b. Titration of the Solution.

10 c.c. are measured into a small beaker, diluted with distilled water, free from ammonia, and the $\frac{N}{10}$ arsenious solution allowed to flow in with constant stirring, until a drop taken out with a glass rod and placed upon iodized starch paper produces no blue stain—towards the end of the process, the faint blue colour produced quickly disappears, therefore the effect must be observed immediately the contact takes place.

Example :—10 c.c. of bromochlorous solution were titrated as described with arsenious solution, and required 13.2 c.c. 55 c.c. also required 72.8 c.c. ; therefore 1 c.c. bromised solution = 1.32 c.c. arsenious solution.

The decinormal arsenious solution is so arranged that 1 c.c. = $\frac{1}{100000}$ at. Cl. Br. or I, and consequently H ; but as 1 atom of NH^3 yields 3 at. H. 3 c.c. of arsenious solution represents $\frac{1}{100000}$ at. ammonia or nitrogen ; and therefore 1 c.c. equals respectively

$$\frac{0.0014}{3} = 0.0004666 \text{ gm. N,}$$

$$\text{or } \frac{0.0017}{3} = 0.000566 \text{ gm. } NH^3,$$

from these data it is of course easy to ascertain the relative value of the bromized solution, as respects ammonia or nitrogen, by simply converting the number of c.c. used in any analysis into their value, as $\frac{N}{10}$ arsenious solution, and multiplying by the systematic coefficients given above ; in fact, each analysis expresses itself in this form, since it is the volume of arsenious solution required which represents the amount of ammonia or nitrogen present ; thus in Krockner's experiments, a solution containing 1 gm. pure ammoniac chloride in the litre was used for estimation. The arsenious solution was not strictly decinormal, but was found by titration with $\frac{N}{10}$ iodine solution to be slightly weaker, so that each c.c. represented 0.000439 gm. N, instead of 0.000466 gm. 20 c.c. ammonia solution = 0.02 gm. NH^4Cl , were placed in a beaker diluted with pure distilled water, and 40 c.c. bromised solution added, shaken for 10 minutes to liberate the nitrogen gas,

40 c.c. bromised solution = 52.8 c.c. $\text{N}^2\text{As}^2\text{O}^3$

Arsenious solution required

for residual titration,	40.6 c.c.
	<hr/> 12.2 c.c.

$12.2 \times 0.000439 = 0.00535$ gm. N. Calculation of formula required = 0.00524 gm.N.

c. Treatment of Nitrates.

It has been seen in Harcourt's process, that nitric acid is converted into ammonia by means of zinc or iron in alkaline solution; this, however, occupies some considerable time. If, however, the action takes place in an acid instead of an alkaline solution, the effect is considerably hastened. To this end the authors use a flask fitted with double bulb funnel, into which some dilute sulphuric acid is placed to absorb any traces of ammonia which might otherwise be carried away with the hydrogen.

The weighed or measured nitrate, or substance containing it, is placed in the flask with some zinc and diluted sulphuric acid, then closed with the safety funnel and allowed to stand for an hour; the contents are then transferred to a beaker, the washings of the funnel and flask added, and neutralised with sodic carbonate, then a measured excess of bromo-chlorous solution of known strength added and titrated residually with arsenious solution as before described. A series of experiments by the authors gave very exact numbers, with ammonic nitrate averaging 99.9% instead of 100.

IRON.

Fe = 56.

Factors.

1 c.c. $\frac{\text{N}}{10}$ permanganate, bichromate	
or hyposulphite	= 0.0056 Fe
" " "	= 0.0072 FeO
" " "	= 0.0080 Fe^2O^3
" " "	= 0.0392 Double iron salt.

§ 40. THE estimation of iron has already been described in § 27. The present section is an amplification of the methods there given, as applied to ores and products of iron manufacture, but before applying the permanganate or bichromate process to these substances, it will be well to notice the direct titration of iron in the ferric

state, by means of stannous chloride and sodic hyposulphite—the two first being available only when the iron is in the ferrous state.

DIRECT TITRATION OF IRON BY STANNOUS CHLORIDE.

§ 41. THE reduction of iron from the ferric to the ferrous state by this reagent has been previously referred to, and it will be readily seen that the principle involved in the reaction can be made available for a direct estimation of iron, being, in fact, simply a reversion of the ordinary process by permanganate and bichromate. In the case of these two reagents, the amount of oxygen *given up* by them is the measure of the quantity of iron, whereas with stannous chloride and hyposulphite, it is the amount *taken up* by them that answers the same purpose.

Fresenius (in his "Zeitschrift für Analytische Chemie," part 1, page 26) has recorded a series of experiments made on the weak points of this process, and gives it as his opinion, that it is most accurate and reliable with proper care, without which, of course, no analytical process whatever is worth anything. The summary of his paper is as follows :—

a. A solution of ferric oxide of known strength is first prepared, by dissolving 10·03 gm. fine pianoforte wire (= 10 gm. pure iron) in pure hydrochloric acid, adding potassic chlorate to complete oxidation, boiling till the excess of chlorine is removed, and diluting the solution to 1 litre.

b. A clear solution of stannous chloride, of such strength that about equal volumes of it and the iron solution are required for the complete reaction. See § 30. 3.

c. A solution of iodine in potassic iodide, containing about 0·005 gm. iodine in 1 c.c. (if the operator has the ordinary decinormal iodine solution at hand, it is equally applicable). The operations are as follows :—

1. 1 or 2 c.c. of the tin solution are put into a beaker with a little starch liquor, and the iodine solution added from a burette till the blue colour occurs ; the quantity is recorded.

2. 10 c.c. of the iron solution = 0·1 gm. iron, are put into a small flask with a little hydrochloric acid, and heated to gentle boiling (preferably on a hot plate), the tin solution is then allowed to flow in from a burette until the yellow colour of the solution is nearly destroyed, it is then added drop by drop, waiting after each addition until the colour is completely gone and the

reduction ended. If this is carefully managed, there need be no more tin solution added than is actually required; however, to guard against any error in this respect, the solution is cooled, a little starch liquor added, and the iodine solution added by drops until a permanent blue colour is obtained. As the strength of the iodine solution compared with the tin has been found in 1, the excess of tin solution corresponding to the quantity used is deducted from the original quantity, so that by this means the volume of tin solution corresponding to 0.1 gm. iron is found.

The operator is, therefore, now in a position to estimate any unknown quantity of iron which may exist, in a given solution, in the state of peroxide, by means of the solution of tin.

If the iron should exist partly or wholly in the state of ferrous oxide, it must be oxidised by the addition of potassic chlorate, and boiling to dissipate the excess of chlorine, as described in 2.

Example: 10 c.c. of iron solution, containing 0.1 gm. iron, required 15 c.c. of tin solution.

A solution, containing an unknown quantity of iron was then taken for analysis, which required 12 c.c., consequently a rule of three sum gave the proportion of iron as follows:—

$$15 : 0.1 \text{ gm.} :: 12 : 0.08 \text{ gm.}$$

It must be remembered that the solution of tin is not permanent, consequently it must be tested every day afresh. Two conditions are necessary in order to ensure accurate results.

1st. The iron solution must be tolerably concentrated, since the end of the reduction by loss of colour is more distinct; and further, the dilution of the liquid to any extent interferes with the quantity of tin solution necessary to effect the reduction. Fresenius found that by diluting the 10 c.c. of iron solution with 30 c.c. of distilled water, 0.1 c.c. more was required than in the concentrated state. This is, however, always the case with stannous chloride in acid solution, and constitutes the weak point in Streng's method of analysis by its means; it would seem that dilution either predisposed it to rapid oxidation, or that water had the power within itself to communicate a certain proportion of oxygen to it.

2nd. The addition of the tin solution to the iron must be so regulated that only a very small quantity of iodine is necessary to estimate the excess—if this is not done another source of error steps in, namely, the influence which dilution, on the one hand, or the presence of great or small quantities of hydrochloric acid on the

other, are known to exercise over this reaction ; practically, it was found that where the addition of tin, to the somewhat concentrated iron solution, was cautiously made so that the colour was just discharged, the mixture then rapidly cooled, starch added and iodine till blue, that the estimation was as reliable as by any other method.

The following examples are from Fresenius.

The standard iron solution contained 10 gm. in the litre ; 10 c.c. were therefore equal to 0.1 gm. iron. 1 c.c. tin solution required 3.62 c.c. iodine.

Exp. 1. 9.97 c.c. of the above iron solution required 11.6 c.c. tin solution and 1.23 c.c. iodine.

Exp. 2. 9.87 c.c. iron solution required 11.26 c.c. tin and 0.44 c.c. iodine. Calculated for 0.1 gm. iron, the above experiments show that—

1	=	11.294	c.c. tin solution
2	=	11.287	„ „
<hr/>			
Mean		11.2905	„ „

3.8204 gm. brown hematite ore was heated with concentrated hydrochloric acid until decomposed, then diluted somewhat, filtered, and the solution made up to 500 c.c.

Exp. 1. 100 c.c. required 43.69 c.c. tin solution and 0.26 c.c. iodine.

Exp. 2. 100 c.c. required 44.15 c.c. tin and 2.12 c.c. iodine, therefore,—

1	=	43.62	c.c. tin solution
2	=	43.57	„ „
<hr/>			
Mean		43.60	„ „

The following equation expresses the result :—

11.2905 SnCl_2 : 0.1 Fe :: 43.60 : $x = 0.3862$ gm. iron in 100 c.c., or 50.54 per cent. of iron in the ore.

A determination of the iron, in the same sample of ore, by permanganate, executed with the greatest care, gave 50.58 per cent.

TITRATION OF IRON BY SODIC HYPOSULPHITE.

§ 42. SCHERER first suggested the direct titration of iron by hyposulphite, which latter was added to a solution of ferric chloride until no further violet colour was produced. This was found by many to be inexact, but Kremer (*Journ. f. Pract. Chem.*, 84, 339) has made a series of careful experiments, the result of which is that the following modified method can be highly recommended.

The reaction which takes place between sodic hyposulphite and ferric chloride is such as to produce ferrous chloride, sodic tetrathionate, and sodic chloride. $2\text{S}^2\text{O}_3\text{Na}^2 + \text{Fe}^2\text{Cl}^6 + 2\text{HCl} = \text{S}^4\text{O}_6\text{H}^2 + 4\text{NaCl} + 2\text{FeCl}^2$. The hyposulphite, which may conveniently be of $\frac{N}{10}$ strength, is added in excess, and its amount determined by $\frac{N}{10}$ iodine and starch liquor.

Process: The iron solution, containing not more than 1 per cent. of metal, which must exist in the ferric state without any excess of oxidising material (best obtained by adding concentrated potassic permanganate until the red colour is produced, then boiling till both that and any free chlorine is expelled), is moderately acidified with hydrochloric acid, sodic acetate added till the mixture is red, then dilute hydrochloric acid until the red colour disappears; then diluted till the iron amounts to $\frac{1}{4}$ or $\frac{1}{2}$ per cent., and $\frac{N}{10}$ hyposulphite added in excess, best known by throwing in a particle of potassic sulphocyanide after the violet colour produced by the hyposulphite has disappeared; if any red colour occurs, more hyposulphite must be added. Starch liquor and $\frac{N}{10}$ iodine are then used to ascertain the excess of hyposulphite; each c.c. of the latter is equal to 0.0056 gm. iron. A mean of several experiments gave 100.06 Fe, instead of 100.

1. Oudemanns' Method.

A simpler process for the direct titration of iron by hyposulphite has been devised by Oudemanns (*Zeitschrift für an. Chem.* vol. vi. p. 129, and the same, vol. ix. p. 342), which gives very good results.

Analytical process: To the ferric solution, which should not contain a large portion of free hydrochloric acid, 3 c.c. of 1 per cent. solution of cupric sulphate is added, 2 c.c. of concentrated hydrochloric acid, and to about every 100 c.c. of fluid, 1 c.c. of a 1 per cent. solution of potassic sulphocyanide.

The mixture may with advantage be slightly warmed, and the hyposulphite delivered in from the burette at first pretty freely—the red colour produced by the sulphocyanide gradually fades away; as this occurs, the hypo must be added in smaller quantities, constantly agitating the liquid until it becomes as colourless as pure water. If any doubt exists as to the exact ending, a slight excess of hyposulphite may be added, and the quantity found by $\frac{N}{10}$ iodine and starch.

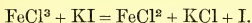
The accuracy of the process is not interfered with by the presence of salts of the alkalis, strontia, lime, magnesia, alumina, or manganoous oxide; neither do salts of nickel, cobalt, or copper, unless their quantity is such as to give colour to the solution.

Oudemanns believes that the small proportion of copper solution added has a kind of catalytic effect in determining the reduction of the iron. This appears, however, doubtful, since Popp (*Zeitschrift für Chem. von Beilstein*, No. 11, 1870), states that equally good effects are obtained by omitting the copper and heating the solution to 40° C. The original process with copper does not necessarily require any heating, and this favours Oudemanns' view.

The results obtained by the author were very satisfactory, when tried side by side with the other well-known processes.

2. Estimation by Potassic Iodide and Sodid Hyposulphite.

When ferric chloride is digested with potassic iodide in excess, iodine is liberated which dissolves in the free potassic iodide—



The free iodine is titrated with hyposulphite and starch, 1 c.c. $\frac{N}{10}$ hypo = 0.0127 gm. I., or 0.0056 gm. Fe.

Analytical process: The solution, which must contain all the iron in the ferric state, is nearly neutralised with caustic potash or soda, transferred to a well-stoppered flask, and some strong solution of potassic iodide added in sufficient quantity to keep all the liberated iodine dissolved; the flask is then heated on the water-bath, closely-stoppered, for about twenty minutes; should there, at the end of this time, be any undissolved iodine remaining, more iodide is added, and the flask cooled, starch liquor added and titrated with hypo till the blue colour disappears.

IRON ORES.

§ 43. In the analysis of iron ores it is very often necessary to determine not only the total amount of iron, but also the state in which it exists; for instance, magnetic iron ore consists of a mixture of the two oxides in tolerably definite proportions, and it is sometimes advisable to know the quantities of each.

In order to prevent, therefore, the further oxidation of the protoxide, and so leading to false results, the little flask apparatus (fig. 26) adapted by Mohr is highly recommendable.

The left hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid is added ; the other flask contains distilled water only, the tube from the first flask entering to the bottom of the second. When the ore is ready in the flask and the tubes fitted, hydrochloric acid is poured in, and a few grains of sodic bicarbonate added to produce a flow of carbonic acid ; the air of the flask is thus dispelled, and as the acid dissolves the ore, the gases evolved drive out in turn the carbonic acid, which is

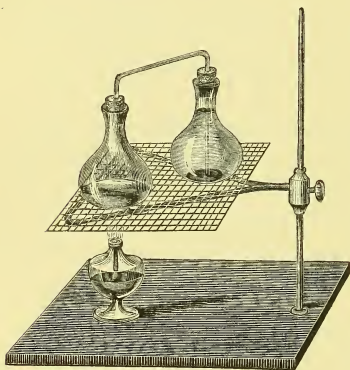


Fig. 26.

partly absorbed by the water in the second flask. When the ore is all dissolved and the lamp removed, the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that, in the majority of cases, it is ready for immediate titration ; if not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added.

When the total amount of iron present in any sample of ore has to be determined, it is necessary to reduce any peroxide present to the state of protoxide by zinc, or stannous chloride, as previously described.

Magnetic Iron Ore.

§ 44. The ferrous oxide is determined first by means of the apparatus, fig. 26, or, instead of the two flasks, one only may be used, or a wide and long test tube ; in either case a cork containing a small bent tube is inserted. The ore is put into the vessel in a state of fine powder, strong hydrochloric acid added, together with a few grains of sodic bicarbonate, and the bent tube dipped under the surface of some cold distilled water ; heat is now applied gently with the lamp until the ore is dissolved, the heat is then removed, and the water rushes into the tube, diluting and cooling the solution.

It may then be poured out into a larger quantity of water, if necessary, and titrated with potassic bichromate or permanganate.

Example : 0.5 gm. of ore was treated as above, and required 19.5 c.c. of $\frac{N}{10}$ bichromate, which multiplied by 0.0056, gave 0.1092 gm. iron = 0.1404 gm. ferrous oxide = 28.08 per cent.

The ferric oxide was now found by reducing 0.5 gm. of the same ore with zinc, and estimating the total iron present, the quantity of bichromate required was—

$$59 \text{ c.c. } \frac{N}{10} = 0.3304 \text{ gm. total Fe}$$

$$\text{Deduct } 0.1092 \text{ ,, as FeO}$$

$$\text{Leaving } 0.2212 \text{ ,, as Fe}^2\text{O}^3$$

The result of the analysis is, therefore,—

Ferrous oxide	28.08 per cent.
Ferric oxide	63.20 ,,
Difference (Gangue, &c.)	8.72 ,,
					<hr/> 100.00

2. Spathose Iron Ore.

The total amount of ferrous oxide in this carbonate is ascertained direct by solution in hydrochloric acid in a test tube, with cork and bent tube dipped into water to prevent oxidation; or, as the carbonic acid evolved is generally sufficient to expel all air, the dipping under water may be dispensed with. Should the ore be very impure, zinc may have to be added in order to ensure the reduction of all the iron present.

As the ore contains in most cases the carbonates of manganese, lime, and magnesia, these may all be determined, together with the iron, as follows—

A weighed portion of ore is brought into solution in hydrochloric acid, and filtered, if necessary, to separate insoluble silicious matter.

The solution is then boiled, with a few drops of nitric acid to peroxidise the iron, diluted, and sodic carbonate added in sufficient quantity to precipitate the ferric oxide, then sodic acetate, and the whole boiled that the precipitate may become somewhat dense and separate from the liquid; filter, and if necessary, reduce the oxide of iron after careful washing, with zinc, and determine with bichromate or permanganate.

The filtrate containing the other bases is treated with sodic hypo-

chlorite covered and set aside for twenty-four hours in order to precipitate the manganese as hydrated oxide, which is collected and titrated as in § 54.

The filtrate from the last is mixed with ammoniac oxalate to precipitate the lime, which is estimated by permanganate, as in § 57.

The filtrate from the lime contains the magnesia, which may be precipitated with sodic phosphate and ammonia, and the precipitate weighed as usual or titrated with uranium solution, as in § 71, see also § 37.

Red and brown hematites can be examined in a similar manner to the foregoing.

3. Chrome Iron Ore.—a. O'Neill's Process.

This material, which is mainly derived from America, is of great commercial importance, as being the source of potassic bichromate.

The ore varies considerably in quality, some samples being very rich, while others are very poor in chromium. In the case of those tolerably free from gangue, the sample is to be first of all brought into *very fine* powder. About a gramme is rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar; 0.5 gm. is then carefully weighed, and mixed with about 3 gm. of a mixture of dried potassic and sodic carbonate, and fused strongly for twenty minutes in a platinum crucible. The mass is then cooled, lixiviated with warm water, filtered, and the filtrate titrated for chromium as in § 64.

The ferric oxide remaining on the filter is dissolved in hydrochloric acid, diluted and titrated with hyposulphite as in § 42.

When the ore contains a larger proportion of silicious or earthy gangue, or much other impurity, it may be necessary to adopt the following method, modified somewhat from O'Neill's process, ("Chem. News," April 12th, 1862.)

The very finely powdered ore is fused with ten times its weight of potassic bisulphate for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is then transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved; no black residue must occur, otherwise the ore is not completely

decomposed; sodic carbonate is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the ashes and precipitate mixed with about twelve times the weight of the original ore, of a mixture of two parts chlorate potassic and three parts sodic carbonate, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as before.

The oxide of iron remaining on the filter is titrated, if required, as above.

b. Britton's Process.

Britton (Journ. Franklin Institute) adopts the following method:—Reduce the mineral to the finest state of division possible in an agate mortar. Weigh off 0.5 gm. and add to it 4.0 gm. of flux, previously prepared, composed of one part potassic chlorate and three parts soda-lime; thoroughly mix the mass by tritulating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright-red heat for an hour and a half or more. The mass will not fuse, but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and turn the powder into a tall 4 oz. beaker, and add about 18 c.c. of hot water, and boil for two or three minutes; when cold, add 15 c.c. of hydrochloric acid, and stir with a glass rod for a few minutes, till the solid matter, with the exception, probably, of a little silica in a flaky gelatinous state, becomes dissolved. Both the iron and chromium will then be in the highest state of oxidation— Fe^2O^3 and CrO^3 . Pour the fluid into a white porcelain dish of about 20 oz. capacity, and dilute with washings of the beaker to about 3 oz. Immediately after, also, pour cautiously into the dish 1.0 gm. of metallic iron of known purity, or an equivalent quantity of double iron salt, previously dissolved in dilute sulphuric acid, and further diluted with cold water to about 5 oz., to make up the volume in the dish to about 8 oz., then determine, volumetrically, with $\frac{N}{10}$ permanganate, the amount of protoxide of iron remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidised to sesquioxide by the chromic acid. Every one part so oxidised will represent 0.320 of metallic chro-

mium, or 0.4663 of sesquioxide, Cr_2O_3 , in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder, as already directed, dissolve it by adding, first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of hydrochloric acid, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure metallic zinc sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease, and the zinc has become quite dissolved; then nearly fill the tube with *cold* water, acidulated with 1.10th of sulphuric acid, and pour the contents into the porcelain dish, add *cold* water to make up the volume to about 8 oz., and complete the operation with the standard permanganate solution.

ESTIMATION OF THE PERCENTAGE OF PURE IRON IN STEEL, CAST AND WROUGHT IRON, SPIEGELEISEN, &c.

Mohr's Method.

§ 45. Instead of the hitherto common method of separately estimating the impurities in samples of manufactured iron and steel, this process is adapted to the delicate estimation of the iron itself, and is similar in principle to the assay of silver by Gay Lussac's method, that is to say, the analysis is so arranged that the greatest accuracy shall be secured.

The standard solutions of potassic bichromate, of which there are two, are so prepared that 100 c.c. or dm. of the first will exactly convert respectively 1 gm. or 10 grains of iron into peroxide; the second, or decimal solution, is one-tenth the strength of the first.

The solution of bichromate No. 1 is prepared by dissolving 8.785 gm. of the pure salt in 1 litre, or 87.85 grn. in 10,000 grains of distilled water at 16°C . The decimal solution No. 2 is made by taking 100 c.c. of No. 1 and diluting it to 1 litre, or 100 decems to 10,000 grains, therefore—

100 c.c. or dm. of No. 1 = 0.01 gm. or 0.1 grn. iron.

100 c.c. or dm. of No. 2 = 0.001 gm. or 0.01 grn. ditto.

The Analytical Process.

The sample of iron to be examined is reduced to powder in a hardened steel mortar, or if in the form of wire, or in a soft state, cut into small pieces, and exactly 1.050 gm. or 10.50 grn. weighed off; this is brought into a long and wide test tube, or small flask, fitted loosely with a cork, and dissolved in pure hydrochloric or sulphuric acid. When the solution is accomplished, 100 c.c. or dm. of bichromate solution No. 1 (containing 0.8785 gm. or 8.758 grn. of bichromate, which is exactly sufficient to peroxidise respectively 1 gm. or 10 grn. of pure iron) is added; the decimal solution is then added from a small burette, until a drop of the mixture, brought in contact with red prussiate of potash, no longer produces a blue colour; the analysis is then calculated in the usual way.

Examples: 1.05 gm. of Bessemer's steel was dissolved in pure sulphuric acid, 100 c.c. bichromate No. 1 added, and afterwards 39 c.c. of No. 2 required for complete oxidation; consequently there were 1.039 gm. of pure iron contained in the 1.050 gm. taken for analysis; this is equal to 989.4 parts per thousand, or 98.94 per cent.

Instead of the empirical solutions here described, the ordinary decinormal and centinormal solutions of bichromate, or permanganate may be employed with equal accuracy. As 100 c.c. of decinormal solution is equal to 0.56 gm. of pure iron, it is necessary that somewhat more than this quantity of the sample should be weighed, say 0.58 or 0.60 gm. 100 c.c. of decinormal solution then added, and the analysis completed with the centinormal solution.

This system of analysis, in order to express directly the percentage of iron in a given sample, can be arranged in the following manner. A solution of ferrous oxide is prepared by dissolving 7 gm. of the double sulphate of iron and ammonia in distilled water, adding a considerable quantity, say 50 c.c., of pure sulphuric acid, and diluting to 1 litre. 1 c.c. of this solution contains 1 milligramme of iron.

1 gm. of the sample of iron is dissolved, and 100 c.c. of bichromate solution No. 1 added; the excess is then ascertained by the iron solution described above; the quantity so used deducted from the 100 c.c. of bichromate will give the percentage of pure iron direct; the objection to this method is that the iron solution is subject to oxidation.

ESTIMATION OF IRON IN SILICATES.

§ 46. Wilbur and Whittlesey (Chem. News, vol. xxii. p. 2), give a series of determinations of iron existing in various silicates, either as mixtures of ferric and ferrous salts or of either separately, which appear very satisfactory.

The very finely powdered silicate is mixed with rather ^{more} than its own weight of powdered flour spar or cryolite (free from iron), in a platinum crucible, drenched with hydrochloric acid and heated on the water bath until the silicate is all dissolved. During the digestion either carbonic acid gas or coal gas free from H^2S is supplied over the surface of the liquid so as to prevent excess of air—when decomposition is complete (the time varying with the nature of the material), the mixture is diluted and titrated with permanganate in the usual way for ferrous oxide; the ferric oxide can then be reduced by zinc and its proportion found.

COPPER.

$$Cu = 63.5.$$

Factors for converting the quantity of Iron represented by Permanganate or Bichromate into Copper.

1 c. c. $\frac{N}{10}$ solution	=	0.00635 gm. Cu
Iron $\times 1.1314$	=	Copper
„ $\times 1.4171$	=	Cupric oxide
„ $\times 4.453$	=	Crystallised cupric sulphate
Double Iron Salt $\times 0.16163$	=	Copper
„ „ $\times 0.2024$	=	Oxide ditto
„ „ $\times 0.6361$	=	Crystallised sulphate do.

§ 47. So many methods have been proposed for the volumetric estimation of copper that the analyst is bewildered by their number and hardly knows upon which to depend.

My own opinion is that in many cases it is safer and less troublesome to estimate the metal by weight; there are, however, instances where volumetric methods can be applied with advantage, and the following processes are chosen as the best.

1. **Method of separating Copper from any of its Ores for Residues in a pure Metallic state, so that it may be weighed direct or estimated by Volumetric methods.**—(Mohr, somewhat modified.)

The substance must be brought into very fine powder, particularly if it contain sulphur, and about 5 gm. of it weighed, placed in a deep porcelain crucible or capsule about 4 in. in diameter, and covered with a concentrated mixture of nitric and sulphuric acids and water, added cautiously; a larger quantity of nitric acid is necessary when sulphur is present (as in pyrites), than in other cases; a watch glass or another capsule is placed upon the top of that containing the mixture so as to prevent loss by spirting—preferably a large watch glass with a hole drilled in the middle. Heat is then applied to boiling and continued till the mass is nearly dry, the cover is then removed, and if not washed clean by the steam produced in the operation itself, is washed with a small quantity of water into the mass, which is again evaporated to dryness; the heat is then increased until all acid vapours are expelled, and the capsule set aside to cool. In the case of pyrites the heat must be continued long enough to burn the sulphur off, the capsule may then be slightly cooled and nitric acid again added, and the burning repeated; in certain cases this may be necessary a third time in order to oxidise all sulphur and extraneous matter.

By this treatment the copper is obtained as sulphate, the iron mostly as insoluble basic sulphate, lead as insoluble sulphate, antimony and tin also insoluble; zinc, cobalt, and nickel are of no consequence in the following treatment. The cold residue is covered with water and boiled till all soluble matter is extracted, then filtered through a small filter into a weighed platinum dish, the residue being washed clean with boiling water; the dish, with its contents, is then placed on the water-bath or over a small spirit lamp, gently heated, acidified with hydrochloric acid, and a small lump of pure zinc added to reduce the copper to the metallic state; there must be sufficient acid to produce a distinct evolution of hydrogen, and the dish covered with a watch glass to prevent loss of liquid by spirting, the glass afterwards being rinsed into the liquid. The end of the reduction is best known by taking a drop of the supernatant liquid out with a glass rod, and touching the surface of some acidulated sulphuretted hydrogen water contained in a small white capsule; if no brown colour is produced, the reduction is ended and any undissolved zinc can either be removed mechanically with

a pair of forceps, taking care to free it from any adhering copper, or dissolved by the addition of fresh acid. The precipitated copper, if pure and clean, will possess a rose red colour ; it must be quickly washed with boiling water to free it from acid—the first washings should be poured off into a beaker and allowed to settle by themselves, as small particles of copper may accidentally be contained in them ; if so, they must be washed clean and added to the platinum dish. Air should not be admitted to the metallic copper while the acid is present to any great extent. When the washings no longer affect litmus paper, the dish should be placed in an air bath, heated to 100 or 110 C., and dried till the weight is constant—the increase in weight is pure copper. A water-bath may be used for drying the copper, in which case it is preferable to wash it first with strong alcohol.

Instead of a platinum dish porcelain or glass will answer, but more time is required, as there is no galvanic action to hasten the decomposition as with the platinum ; in this case the deposited copper is not attached to the sides or bottom of the vessel.

Instead of drying and weighing the copper it can be dissolved and estimated by Fleitmann's process, or the following modification may be adopted. The solution obtained by digesting the residue of the first operation in water, invariably contains iron, whenever that metal is present in the original substance ; in order to remove it, therefore, the neutral and concentrated solution is boiled with a tolerable quantity of sodic acetate, the insoluble iron precipitate filtered off, washed with boiling water containing sodic acetate, and the copper solution, which must not be too dilute, titrated by De Haen's method, with sodic hyposulphite, or in the absence of manganese, cobalt, nickel, arsenic, mercury, and silver, the solution, without removing the iron, may be titrated direct with potassic cyanide as in § 47. 5, using the precautions there mentioned.

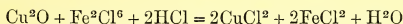
Examples of the accuracy with which copper may be separated from ores and other compounds by precipitation with zinc :—

1 gm. pure metallic copper was mixed with 0·5 gm. each of the following substances, either as metals or salts, viz.:—gold, silver, platinum, tin, lead, iron, zinc, nickel, cobalt, bismuth, arsenic, uranium, mercury, molybdenum, antimony, sulphur, silica, and phosphate of lime, the whole was treated with nitric and sulphuric acids as previously described, and the residue, after one ignition, lixiviated with water, filtered off, and treated with hydrochloric acid to

remove silver, then after filtration, zinc and hydrochloric acid added in a large platinum dish. The yield of pure copper was 0.996 gm.; without recording any further experiments in detail, it may suffice to say that in more than twenty determinations of copper in various combinations, the mean results obtained were 99.7 instead of 100.

2. Schwarz's method (results tolerably accurate).

This process is based upon the fact that grape sugar precipitates cuprous oxide from an alkaline solution of the metal containing tartaric acid; the oxide so obtained is collected and mixed with ferric chloride and hydrochloric acid—the result is the following decomposition:—



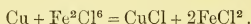
Each atom of copper reduces an atom of ferric chloride to ferrous chloride, which is estimated by permanganate with due precaution. The iron so obtained is calculated into copper by the requisite factor.

Process: The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or flask, and most of the acid in excess saturated with sodic carbonate; neutral potassic tartrate is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue fluid by adding caustic potash or soda in excess; the vessel is then heated cautiously to about 50° C., in the water-bath, and sufficient grape, milk, or starch sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the heat must never exceed 90° C. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterward the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is thoroughly washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of ferric chloride (free from nitric acid or free chlorine) added, together with a little sulphuric acid; the whole is then warmed and stirred until the cuprous chloride is all dissolved. It is then filtered into a good sized flask, the old and new filters being both well washed with hot water, to which, at first, a little free sulphuric acid should be added in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way, bichromate may also

be used, but the end of the reaction is not so distinct as usual, from the turbidity produced by the presence of copper.

3. Fleitmann's Method.

The metallic solution, free from nitric acid, bismuth, or lead, is precipitated with zinc as in § 47. 1 ; the copper collected, washed, and dissolved in a mixture of ferric chloride and hydrochloric acid ; a little sodic carbonate may be added to expel the atmospheric air. The reaction is—



When the copper is all dissolved, the solution is diluted and titrated with permanganate ; 56 iron represent 31.7 copper.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration ; the zinc must be finely divided and the mixture warmed ; the copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water then with weak hydrochloric or sulphuric acid and water, to remove the zinc ; again with water, and then dissolved in the acid and ferric chloride as before.

4. Method of De Haen and E. O. Brown (results accurate in the absence of persalts of iron and other reducible substances).

The solution of the metal, if it contains nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralised with sodic carbonate and acetic acid added, the sulphate solution must be neutral, or only faintly acid ; excess of acetic acid is of no consequence.

The process is based on the fact that when potassic iodide is mixed with a salt of copper in solution, cupric iodide is precipitated as a dirty white powder, and iodine set free. If the latter is then titrated with hyposulphite and starch liquor, the corresponding quantity of copper is found by the systematic factor.

Process : The solution (containing not less than 1 gm. Cu to each 100 c.c.), free from iron, chlorine or free nitric and hydrochloric acids is brought into a beaker or flask, potassic iodide in good quantity added, and the hyposulphite delivered from a burette till the brown colour has disappeared ; starch liquor is then added, and $\frac{N}{10}$ iodine,

to ascertain the excess of hyposulphite, or the titration may proceed direct by adding starch at first, and hyposulphite, till the blue colour is discharged.

Example: 10 c.c. of solution of cupric sulphate, containing 0.39356 gm. = 0.1 gm. copper was mixed with potassic iodide in a beaker, and 19 c.c. of $\frac{N}{10}$ hyposulphite added, then starch liquor, and 3.2 c.c. $\frac{N}{10}$ iodine required to produce the blue colour = 15.8 c.c. hyposulphite; this multiplied by 0.00635 gave 0.1003 gm. copper instead of 0.1 gm.

In order to remove iron from copper solutions, previous to their analysis, it has been recommended to precipitate it with ammonia on the one hand, or to boil with sodic acetate on the other, and precipitating as basic acetate. In neither case can very satisfactory results be obtained, for with ammonia at least three precipitations are necessary to remove all the copper from the ferric oxide; boiling with sodic acetate does not always separate all the iron, and even if it should do so, the precipitate holds the copper tenaciously; the collection of fluid therefore, by these repeated precipitations and washings, is so considerable, that the process cannot be applied, except by evaporation, to a small bulk. The sodic acetate is far preferable to the ammonia; it must, however, be used in large quantity, and the precipitate washed with hot water containing sodic acetate. In certain cases (*i.e.*, where metals may be present which would interfere with the titration of the entire liquid by Parkes' process as described below), it may be advisable to precipitate the iron by ammonia, slightly wash the precipitate, and then push it through the funnel into a white capsule, and titrate with potassic cyanide at once for the slight amount of copper present, adding the weight so found to that obtained in the filtrate by some other method.

5. Method of Parkes and C. Mohr (results tolerably accurate, in the absence of manganese, nickel, cobalt, mercury, and silver).

This well-known and much used process for estimating copper depends upon the decoloration of an ammoniacal solution of copper by potassic cyanide; the reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, ammonic cyanide and formate, (Liebig). Owing to the influence exercised by variable quantities of ammonia, or its neutral salts, upon the

decoloration of a copper solution by the cyanide, it is necessary that the solution analysed should contain pretty nearly the same proportion of ammonia as that upon which the cyanide has been originally titrated, and no heat should be used.

The experiments made by Fresenius show that this is absolutely necessary, and the undermentioned results, obtained by myself, point to the same conclusion.

1. 10 c.c. of solution of cupric sulphate, containing 0.10 gm. Cu, with 1 c.c. of ammonia, spec. grav. .900, required 21.3 c.c. cyanide solution.

2. 50 c.c. of copper solution = 0.50 gm. Cu, and 5 c.c. ammonia, required 106.5 c.c. cyanide.

These agree exactly.

3. 20 c.c. copper solution = 0.20 Cu, with 6 c.c. ammonia, required 43 c.c. cyanide, instead of 42.6.

4. 20 c.c. copper = 0.20 Cu, with 20 c.c. ammonia, required 44 c.c. cyanide instead of 42.6.

The results with salts of ammonia were very similar, but even more marked.

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field, however, has stated that this is not necessary ("Chem. News," vol. i. p. 25), and I can fully endorse his statement that the presence of the suspended oxide of iron is no hindrance to the estimation of the copper, in fact it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange brown; if it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary, to enable the operator to hit the exact point, and it is always well to make use of both indicators. The following experiment is given from among many others.

10 c.c. of copper solution = 0.10 gm. Cu, were put into a small white porcelain dish, and 2 c.c. ammonia, .900 added, then the cyanide cautiously delivered from the burette, till the faintest violet tinge only was perceptible, the quantity so used was 21.3 c.c.; 10 c.c. of copper solution were then put into another dish, a little freshly precipitated ferric oxide added, together with 2 c.c. ammonia. The cyanide was then delivered without looking at the burette

until the oxide had acquired the proper colour; the burette was found to stand at 21·3 c.c., and the clear solution possessed the same faint tint as before.

The solution of potassic cyanide should be titrated afresh at intervals of a few days. Further details of this process are given, § 48.

6. Pelouze's Process (results tolerably accurate, in the absence of tin, nickel, cobalt, or silver).

This process is based on the fact that if an ammoniacal solution of copper is heated from 40° to 80° C., and a solution of sodic sulphide added, the whole of the copper is precipitated as oxysulphide, leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point; special practice, however, will enable the operator to hit the exact point closely.

Preparation of Standard Solutions.

It is first necessary to have a solution of pure copper, of known strength, which is best made by dissolving 39·356 gm. of pure sulphate of copper in 1 litre, or 393·56 grn. in 10,000 grains of distilled water; each c.c. or dm. will respectively contain 0·01 gm. or 0·1 grn. of pure metallic copper.

A measured quantity, say 50 c.c., of standard solution of copper, is freely supersaturated with caustic ammonia, and heated till it begins to boil; the temperature will not be higher than 180°, in consequence of the presence of the ammonia; it is always well, however, to use a thermometer; the sodic sulphide is delivered cautiously from a Mohr's burette, until the last traces of blue colour have disappeared from the clear liquid above the precipitate. The experiment is repeated, and if the same result is obtained, the number of c.c. or dm. required to precipitate the amount of copper contained in 50 c.c. or dm., = 0·5 gm. or 5 grn. respectively, is marked upon the sulphide of sodium bottle. As the strength of the solution gradually deteriorates, it must be titrated afresh every day or two. Special regard must be had to the temperature of the precipitation, otherwise the accuracy of the process is seriously interfered with.

TECHNICAL EXAMINATION OF COPPER ORES.

§ 48. In May 1867 the Directors of the Mansfield Copper Mines offered a premium for the best method of examining these ores, the chief conditions being tolerable accuracy, simplicity of working, and the possibility of one operator making at least eighteen assays in the day.

The fortunate competitor was Dr Steinbeck, whose process satisfied completely the requirements of the Directors. The whole report is contained in Fresenius' "Zeitschrift," part i, 1869, and is also translated in "Chem. News," April 16, 1869. The following is a somewhat condensed *resumé* of the process, the final titration of the copper being accomplished by potassic cyanide as in the previous description. A very convenient arrangement for filling the burette with standard solution is shown in fig. 27, where a series of analyses have to be made, and the burette continually emptied, it may be refilled by simply blowing upon the surface of the liquid.

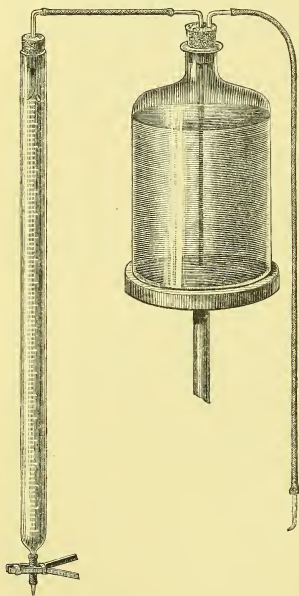


Fig. 27.

a. The Extraction of the Copper from the Ore.

5 gm. of pulverised ore is put into a flask with from 40 to 50 c.c. of crude hydrochloric acid, specific gravity 1.16, whereby all carbonates are converted into chlorides,

while carbonic acid is expelled. After awhile there is added to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1.2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and

bitumen, have to be roasted previous to being subjected to this process ; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a well arranged sand bath for half an hour, and the contents only boiled for about fifteen minutes, after which the whole of the copper occurring in the ore, and all other metals are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or at the most only 0.01 to 0.03 per cent. has been left undissolved.

The extraction of the copper from the ore, according to this method, is complete even in the case of the best quality of ore, which contains about 14 per cent. of metal ; while, at the same time, the very essential condition for the proper and complete separation of the metal—viz., the entire absence of nitric acid, or any of the lower degrees of oxidation of nitrogen, is fully complied with.

b. Separation of the Copper.

The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker glass of about 400 c.c. capacity ; in this beaker has been previously placed a rod of metallic zinc, weighing about 50 gms., and fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate not contain more than from 0.1 to 0.3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is, owing especially also to the complete absence of nitric acid, completely finished in from half to three quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace of copper will be detected ; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must be always employed) has been removed, the spongy metal is repeatedly and carefully washed by decantation with fresh water, which need not be distilled, and care taken to collect together every particle of the spongy mass.

c. Quantitative Estimation of the Precipitated Copper.

To the spongy metallic mass in the beaker glass, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper thus dissolved by the aid also of moderate heat, in the form of cupric nitrate, which, in the event of any small quantity of lead being present, will of course be contaminated with lead.

When copper ores are dealt with, which contain above 6 per cent. of copper, which may be somewhat judged from the rather larger bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are applied for dissolving the spongy metallic mass. The solution thus obtained is left to cool, and next mixed, immediately before titration with potassic cyanide, with 10 c.c. of normal solution of liquid ammonia, prepared by diluting 1 volume of liquid ammonia, sp. gr. 0.93, with 2 volumes of distilled water.

In the case of such ores as yield over 6 per cent. of copper, and when a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then exactly divided into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue coloured solution only contains besides ammonic nitrate any lead which might have been dissolved having been precipitated as hydrated oxide of lead, which does not interfere with the titration with cyanide. The solution of the last-named salt is so arranged, that 1 c.c. thereof exactly indicates 0.005 gm. of copper. Since, for every assay, 5 gms. of ore have been taken, 1 c.c. of the titration fluid is, according to the following proportion:—

$$5 : 0.005 :: 100 : x = 0.1,$$

equal to 0.1 per cent. of copper; it hence follows that, by multiplying the number of the c.c. of cyanide solution used to make the blue colour of the copper solution disappear by 0.1, immediately indicates the percentage of copper contained in the ore.

Steinbeck tested his method specially, in order to see what influence is exercised thereupon by (1) ammonic nitrate, (2) caustic ammonia, (3) presence of lead. The copper used for the experiments for this purpose was pure metal, obtained by galvanic action,

and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. 5 gm. of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of normal nitric acid, the flask gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. 30 c.c. of this solution were always applied to titrate one and the same solution of potassic cyanide under all circumstances. When 5 gm. of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·150 gm. of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 gms. of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of normal nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

The influence of double quantities of ammoniac nitrate and free caustic ammonia (the quantity of copper remaining the same), is shown as follows :—

(a.) 30 c.c. of the normal solution of copper, containing exactly 0·150 gm. of copper, were rendered alkaline with 10 c.c. of normal ammonia, and are found to require, for entire decoloration, 29·8 c.c. of cyanide solution; a second experiment, again with 30 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average is 29·85 c.c.

(b.) When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia, instead of only 8, whereby the quantity of free ammonia and of ammoniac nitrate is made double what it was in the case of *a*, there is required of the very same cyanide solution 30·3 c.c. to produce decoloration. A repetition of the experiment, exactly under the same conditions, gave 30·4 c.c. of the cyanide solution employed; the average of both is, therefore, 30·35 c.c.

The difference between 30·35 and 29·85 is equal to 0·5 c.c., and that figure is therefore the coefficient for the influence of double quantities; and supposing this to happen with the ores in question, it would only be equivalent to 0·05 per cent. of metallic copper. It is hence clear that slight aberrations of from 0·1 to 0·5 c.c. in the measuring out of 8 c.c. of normal nitric acid, used to dissolve the spongy copper, and of 10 c.c. of normal ammonia, in order to render that nitric acid copper solution alkaline, is of no consequence what-

ever for the technical results to be deducted from the assay ; it should be, moreover, borne in mind that the quantities of free ammonia and of nitrate in the actual assay of ores, for which always a quantity of 5 gms. of ore is taken, varies according to the richness or poverty of the ores in copper.

The quantitative aberrations between ores containing 1 per cent. or 6 per cent. of metal, vary very little from the normal quantities exhibited by ores containing 3 per cent. of metal. The relation is as 1 : 2 ; and, for technical purposes, this has been proved not to be a disturbing quantity.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of cyanide, and especially when carbonate, sulphate, and, worse still, ammonic chloride are simultaneously present, these salts exert a very disturbing influence, see § 46·5. The presence of oxide of lead in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness with the blue tint ; but the presence of this oxide does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess ; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Steinbeck purposely made some experiments to test this point, and his results show that a moderate quantity of lead has no influence.

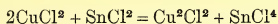
Experiments were also carefully made to ascertain the influence of zinc, the result of which showed that up to 5 per cent. of the copper present the zinc had no disturbing action, but a considerable variation occurred as the percentage increased. Care must therefore always be taken in washing the spongy copper precipitated from the ore solution by means of zinc.

The titration must always take place at ordinary temperatures, since heating the ammoniacal solution while under titration to 40 or 45° C., reduces the necessary quantity of cyanide considerably.

ESTIMATION OF COPPER AND IRON TOGETHER IN MINERALS (RICH CUPREOUS PYRITES, &c.) BY STANNOUS CHLORIDE AND PERMANGANATE—WEYL.

§ 49. This process is based on the fact, that a solution of a cupric salt in excess of hydrochloric acid at a boiling heat, shows, even when the smallest trace is present, a greenish yellow colour. If to

such a solution stannous chloride is added in excess, a colourless cuprous chloride is produced, and the loss of colour indicates the end of the process.



The change is easily distinguishable to the eye, but should any doubt exist as to whether stannous chloride is in excess—a small portion of the solution may be tested with mercuric chloride, any precipitate of calomel indicates the presence of stannous chloride.

In the case of pyrites where iron is also present, the quantity of tin solution required will of course represent both the iron and the copper—in this case a second titration of the original solution is made with permanganate, and the quantity so found is deducted from the total quantity—the amount of tin solution corresponding to copper is thus found.

The tin solution is prepared as described in § 30.3.

A standard copper solution may be made of any convenient strength by dissolving pure cupric sulphate in distilled water, and diluting to a definite volume.

Process: A volume of the copper solution = 0.1 gm. Cu. is put into a white glass flask, 5 c.c. pure strong hydrochloric acid added placed on a sand bath and brought to boiling heat, the tin solution is then quickly delivered in from a burette until nearly colourless, finally a drop at a time till perfectly so; 5 c.c. more of acid is then added, and should this produce any return of colour, more tin solution is required to remove it. The total quantity is noted.

The sample of ore is prepared in the usual way by treatment with nitric acid and afterwards with sulphuric or hydrochloric acid to remove the nitric. Silica, lead, tin, antimony, silver, or arsenic, are of no consequence, as when the solution is diluted with water to a definite volume, the precipitates of these substances settle to the bottom of the measuring flask, and the clear liquid may be taken out for titration.

Process for ores containing copper and iron. Example: 4 gm. ore was prepared and diluted to 250 c.c., 25 c.c. required 26.75 c.c. tin solution whose strength was 16.2 c.c. for 0.1 gm. Cu.

25 c.c. of ore solution were diluted, warmed, zinc and platinum added till reduction was complete, and titrated with permanganate whose quantity = 0.0809 gm. Fe.

The relative strength of the tin solution to iron is 18·34 c.c. = 0·1 gm. Fe—thus :

$$\begin{array}{rclcl}
 \text{at : wt. Cu} & \text{at wt. Fe} & = & \text{Cu} & : & x \text{ Fe} \\
 63\cdot5 & 56 & = & 0\cdot1 & : & 0\cdot0883 \\
 \text{therefore } 0\cdot1 \text{ gm. Cu} & = & 0\cdot0883 \text{ gm. Fe} & = & 16\cdot2 \text{ c.c. SnCl}^2 \\
 \text{whence } 0\cdot0883 : 0\cdot1 & = & 16\cdot2 : 18\cdot34 \\
 \text{thus } 0\cdot0809 \text{ Fe (found above)} & = & 14\cdot837 \text{ c.c. SnCl}^2 \\
 0\cdot1 : 0\cdot0809 & = & 18\cdot34 : 14\cdot837
 \end{array}$$

Calculation of Results.

$$\begin{array}{rcl}
 \text{Iron and copper} & = & 26\cdot750 \text{ c.c. SnCl}^2 \\
 \text{Subtract for iron} & = & 14\cdot837
 \end{array}$$

$$\text{Leaving for copper} \quad 11\cdot913$$

25 c.c. of ore solution therefore contained $16\cdot2 : 0\cdot1 = 11\cdot913 : 0\cdot0735$ gm. Cu, and as 4 gm. ore = 250 c.c. contained of course 0·735 gm. Cu = 18·38% Cu. Analysis by weight as a control gave 18·34% Cu.

Fe volumetrically 20·25%, by weight 20·10%.

The process is only fit for technical purposes, and not available for very weak solution of copper or for poor ores.

Galetti advocates the use of standard potassic ferrocyanide for estimating both copper and zinc in weak acetic solution, full details of which are contained in Fresenius Zeitschrift, vol. iv. p. 213, and vol. viii. 135, the latter also in Chem. News, vol. xx. p. 242.

The process is capable of tolerably accurate results after considerable practice; the principle is explained in the following section on zinc.

ZINC.

$$\text{Zn} = 65.$$

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{ solution} = 0\cdot00325 \text{ gm. Zn.}$$

$$\begin{array}{rclcl}
 \text{Metallic iron} & \times & 0\cdot5809 & = & \text{Zinc.} \\
 \text{,,} & \times & 0\cdot724 & = & \text{Zinc oxide.} \\
 \text{Double iron salt} & \times & 0\cdot08298 & = & \text{Zinc.} \\
 \text{,,} & \times & 0\cdot1034 & = & \text{Zinc oxide.}
 \end{array}$$

1. Method of C. Mohr (results accurate in the absence of manganese and the heavy metals in general).

§ 50. In the article on the analysis of potassic ferridcyanide, by Lenssen's method, § 57, it is shown that greater exactness may be obtained through the use of an excess of zinc in the mixture, so that the iodine liberated shall be the true measure of the substance.

In the present method the process may be considered to be reversed :—with an excess of ferridcyanide the liberated iodine shall, express the true quantity of zinc sought.

If to a solution of zinc in acetic acid an excess of potassic ferridcyanide is added, a reddish yellow precipitate of ferridcyanide of zinc occurs, having the composition, $(\text{Cy}^6\text{Fe})_3\text{Zn}^2$.

If now to this mixture an excess of potassic iodide be added, the decomposition occurs as follows. $3\text{Zn}^2(\text{Cy}^6\text{Fe})^2 + 4\text{H}\bar{\text{A}} + 4\text{KI} = 3\text{Zn}^2\text{Cy}^6\text{Fe} + 4\bar{\text{K}}\text{A} + \text{H}^4\text{Cy}^6\text{Fe} + \text{I}^4$. Each equivalent of iodine found by $\frac{\text{N}}{10}$ hyposulphite = 0.00975 gm. zinc.

The process is as follows :—

The metal and its compounds must exist in an acetic acid solution, which is best managed by dissolving the ores in *aqua regia*, evaporating to dissipate the excess of acid, neutralising the remainder with sodic carbonate, then adding a strong solution of sodic acetate in excess, and boiling ; then filter and wash with boiling water containing a little sodic acetate ; iron is removed by this means but not manganese, so that should the latter be present the process will not be applicable. In the presence of other metals the zinc must be separated as sulphide or oxide, and afterward brought into solution in acetic acid.

To the acetic acid solution so prepared a freshly-made solution of potassic ferridcyanide is added in slight excess, (known by a drop of the mixture giving a blue colour with ferrous salts), potassic iodide in sufficient quantity is then added, together with starch liquor, and the titration with $\frac{\text{N}}{10}$ hyposulphite performed as usual—the greenish blue colour of the mixture entirely disappears, and gives place to the pure yellow of the red prussiate of potash, when in solution.

Fr. and C. Mohr and Fresenius have found the method tolerably reliable. I have also found the same with pure zinc salts, it is not necessary, therefore, to give examples further than to say that in the case of pure salts of zinc 99.8 and 100.12 were obtained instead of 100,—it is doubtful if the process is worth much in treating impure ores of zinc.

2. Schwarz's Method (results accurate).

The principle of this method is based on the fact that when zinc sulphide is mixed with ferric chloride and hydrochloric acid—ferrous chloride, zinc chloride, and free sulphur are produced : if the ferrous chloride is estimated with permanganate or bichromate, the propor-

tional quantity of zinc present is ascertained, 2 at Fe, represent 1 at Zn.

Ores of zinc are treated with hydrochloric, or in the case of blende, with that and nitric acid, dissolved, evaporated to dissipate excess of acid, and then precipitated with a mixture of carbonate and caustic ammonia, and digested warm till all the zinc precipitate is dissolved, the residue is washed with ammoniacal water and the filtrate and washings mixed. This ammoniacal solution (which should contain all the zinc), is then warmed, and the zinc precipitated with a slight excess of sodic or ammonic sulphide; when the precipitate has subsided the clear liquid is passed through a tolerably large and porous filter, the precipitate brought upon it, and well washed with warm water containing ammonia, till the washings no longer discolour an alkaline lead solution.

The filter with its contents is then pushed through the funnel into a good sized flask containing a sufficient quantity of ferric chloride mixed with hydrochloric acid, immediately well stopped or corked, gently shaken, and put into a warm place; after some time it should be again well shaken, and set aside quietly for about 10 minutes. After the action is all over the mixture should possess a yellow colour from the presence of undecomposed ferric chloride; when the cork or stopper is lifted there should be no smell of sulphuretted hydrogen. The flask is then nearly filled with cold distilled water, some dilute sulphuric acid added, and titrated with permanganate or bichromate as usual. The free sulphur and filter will have no reducing effect upon the permanganate if the solution is cool and very dilute.

Example: 1 gm. pure zinc oxide was dissolved in hydrochloric acid, supersaturated with ammonic sulphide, the precipitate well washed and digested with acid ferric chloride, the whole was diluted to 500 c.c. in a stoppered flask, 100 c.c. titrated with permanganate of such strength that 120 c.c. = 1 gm. iron. 33.4 c.c. were required = 0.278 gm. iron, this multiplied by 5, as $\frac{1}{5}$ only was taken, gave 1.390 gm. iron, which multiplied by the factor for zinc oxide 0.724 gave 1.0063 gm. instead of 1 gm.

Another 100 c.c. titrated with $\frac{N}{10}$ bichromate, required 49.3 c.c. which multiplied by the $\frac{N}{10}$ factor, 0.00453 gave 0.1998129 gm. $\times 5 = 0.9990$ gm. ZnO.

3. Precipitation by Standard Sodid Sulphide, with Alkaline Lead Solution as Indicator, applicable to most Zinc Ores and Products (results accurate).

The ammoniacal solution of zinc is prepared just as previously described in Schwarz's method.

The standard sodid sulphide is best made by saturating a portion of caustic soda solution with sulphuretted hydrogen, then adding sufficient soda solution to remove the smell of the free gas, and diluting the whole to a convenient strength for titrating.

The standard zinc solution is best made by dissolving 44.12 gm. of pure zinc sulphate to the litre, or 441.2 gm. to the 10,000 grns.; 1 c.c. or dm. will then contain 0.010 gm. or 0.10 grn. of metallic zinc, and upon this solution, or one prepared from pure metallic zinc of the same strength, the sulphide solution must be titrated.

The alkaline lead solution used as indicator is made by heating acetate of lead, tartaric acid, and caustic soda solution in excess together until a clear solution is produced. It is preferable to mix the tartaric acid and soda solution first, so as to produce sodid tartrate, or if the latter salt is at hand it may be used instead of tartaric acid.

The Analytical Process.

50 c.c. of zinc solution = 0.5 gm. Zn are put into a beaker, a mixture of solutions of ammonia and ammonic carbonate (3 of the former to about 1 of the latter), added in sufficient quantity to redissolve the precipitate which first forms. A glass rod is then dipped into the lead solution and with it a few drops, placed at some distance from each other, on filtering paper, placed upon a slab or plate.

The solution of sodid sulphide contained in an ordinary Mohr's burette is then suffered to flow into the zinc solution until, on bringing a drop from the mixture and placing it upon the filtering paper so that it may expand and run into the drop of lead solution, a black line occurs at the point of contact, the reaction is very delicate; at first it will be difficult, probably, to hit the exact point, but a second trial with 25 or 50 c.c. of zinc solution will enable the operator to be certain of the corresponding strength of the sulphide solution. As this latter is always undergoing a slight change, it is necessary to titrate occasionally.

Direct titration with pure zinc solution gave 99.6 and 100.2, instead of 100.

Groll recommends the use of protochloride of nickel as indicator,

instead of nitroprusside of sodium or lead. The drops are allowed to flow together on a porcelain plate; while the point of contact shows a blue or green colour the zinc is not all precipitated by the sodic sulphide, therefore, the latter must be added until a grayish black colour appears at contact. I do not see any advantage over the lead paper in the process.

COROLLARY.

Estimation of Alkaline Sulphides by Standard Zinc Solution.

§ 51. This method, which is simply a counterpart of the foregoing, is especially applicable for the technical determination of alkaline sulphides in impure alkalis, mother liquors, &c.

If the zinc solution be made by dissolving 3.253 gm. pure metallic zinc in hydrochloric acid, supersaturating with ammonia, and diluting to a litre, or 32.53 gm. to 10,000 grns.* 1 c.c. or dm. will respectively indicate—

0.0016	gm. or 0.016 grn. sulphur
0.0039	„ or 0.039 „ sodic sulphide
0.00551	„ or 0.0551 „ potassic sulphide
0.0034	„ or 0.034 „ ammoniac sulphide

The zinc solution is added from a burette until a drop, brought in contact with the lead solution on filtering paper, no longer gives a black stain at the edges.

Estimation of Zinc as Ferrocyanide. (Galetti.)

§ 52. When ores containing zinc and iron are dissolved in acid, and the iron precipitated with ammonia, the ferric oxide invariably carries down with it a portion of zinc; by this new process the zinc is converted into soluble acetate and titrated by a standard solution of potassic ferrocyanide.

Galetti applies the same process to the estimation of copper, but varying the strength of the standard solutions, which are both empirical.

The potassic ferrocyanide for Copper contains 50.225 gm. per litre
For Zinc 41.250 gm. per litre,

therefore	1 c.c. = 0.01 gm. Cu
	1 c.c. = 0.01 gm. Zn

I have not been able to see the author's original paper, and, therefore, cannot tell how the process ends. I suppose by bringing a drop of the solution to which the ferrocyanide has been

added to precipitate the zinc, in contact with a drop of some ferric solution on filter paper or white plate, any blue colour occurring shows an excess of the precipitant.*

The paper contained in the "Zeitschrift" above quoted and translated into the *Chemical News* is by no means lucid, and gives no examples whatever of correctness; the statement, however, is made that it is adopted by several known analysts for the estimation of zinc in calamine ores from Sardinia as being best adapted to the purpose. A somewhat condensed translation of the paper is as follows:—The process can be used for both copper and zinc in two ways, according to the pleasure of the operator as to whether the titration shall occur with or without the presence of the ferric oxide, if this has to be filtered away some considerable time is expended, but greater accuracy is secured.

In the case of copper pyrites, the procedure is as follows:—Take 1 gm. of the previously very carefully pulverised and dried ore. Treat it first with concentrated nitric acid, boiling to incipient dryness, in order thereby to free the sulphur from any small particles of ore which are at first taken up by it. Add 10 c.c. of hydrochloric acid, boil down to about half that bulk, dilute with distilled water, add ammonia in large excess; boil the fluid, add pure acetic acid (sp. gr., 1.070) until the liquid assumes an emerald-green colour. After the liquid has been well stirred up, boil again for about two minutes; then add again ammonia in excess. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to $\frac{1}{2}$ litre. This having been done, the fluid is cautiously acidified with very dilute acetic acid, 1 part of the acid just alluded to, and 10 parts of distilled water. A large excess should be avoided; the fluid should only be slightly acid. As soon as the basic ferric acetate has subsided, the precipitation of the copper by means of the standard solution of ferrocyanide proceeded with.

Since the cupric oxide which might have adhered to the ferric oxide has been converted by the process just described into a soluble salt, it cannot fail to be completely precipitated by the ferrocyanide solution. When a determination of copper has to be made in ores which are rather poor (that is to say, contain less than, or up to 6 per cent. of copper), it is preferable to add to the nitric acid solution

* I since find that the author depends upon the change of colour from white to greyish white (see p. 141).

0.1 gm. of pure copper, which quantity has to be deducted afterwards from the results obtained. This precaution is required in order to prevent the presence of a large quantity of oxide of iron from vitiating the results of analysis of poor ores. When ores contain up to 12 per cent. of copper, a quantity of 1 gm. of the ore should be taken; but, for richer ores, 0.5 gm. is sufficient. It is always advisable to make a control analysis with pure copper at the same time while testing the ores, and precisely under the same conditions of dilution and temperature.

The second modification without the presence of ferric oxide is carried out in the following manner.

After the second addition of ammonia to the liquid, it is filtered, and the precipitate is washed with a dilute and boiling solution of acid ammoniac acetate. This solution is prepared by saturating 20 gms. of pure acetic acid with ammonia, and addition thereto of 15 gms. of pure acetic acid in 585 gms. of water. When the washing of the ferric oxide is carefully done, the salt of copper, which tenaciously adheres to the oxide, is entirely removed therefrom; but it will require about 400 gms. of the fluid, the preparation of which has just been described.

The normal solution of copper should be treated as follows:—

For controlling the titration, 0.2 gm. of pure copper is dissolved in nitric acid; excess of ammonia is added; the fluid next acidified with acetic acid, thereupon diluted with 400 gms. of acid ammoniac acetate, and the whole brought up to 500 gms. To this solution 20 c.c. of the standard solution of potassic ferrocyanide are added, and, after the necessary corrections have been made, the liquid must not contain any excess of either copper or of ferrocyanide.

Zinc ores are treated in the same manner as just described for copper ores. When zinc sulphide (the “black-jack” of English miners) is to be operated upon, care should be taken that, after the addition of hydrochloric acid, the fluid should be sufficiently evaporated as to ensure the expulsion of all nitric acid. Since zinc ores are usually rather rich, $\frac{1}{2}$ gm. is sufficient for analysis. Calamine-stone (native zinc carbonate) should at once be acted upon with hydrochloric acid; but, in order to make sure of the complete oxidation of all the iron the ore may happen to contain, it is best to add to the acid a few decigrammes of pure potassic chlorate. After having suffered this solution to boil for a few minutes, it is diluted with distilled water; a large excess of ammonia is added to the solution, and it is next treated as above described for copper.

The author states that he has convinced himself, by a set of experiments instituted on purpose, that the presence of compounds of lead (as, for instance, carbonate, sulphate, and sulphide of lead) occurring with the ores of zinc, does not interfere with the correctness of the complete precipitation of zinc as ferrocyanide. This even holds good up to 10 per cent of metallic lead, a quantity which does not, also, interfere when mixed with copper ores.

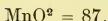
Since some ores of zinc, especially calamine-stone, may, and often do, contain manganese, it is best to add to the ammoniacal solution, before any acetic acid is added, a few drops (from two to four) of bromine, in order to convert thereby the manganous oxide into manganic, leaving the solution standing for twenty-four hours after the addition of the bromine.

Since the ammoniacal solution of chloride of zinc is colourless, there should be added to it, previous to the very cautious acidification by means of dilute acetic acid, a few drops of tincture of litmus, in order to more readily hit the precise point of sufficient acidification, to be exhibited by the blue colouration changing to red.

When iron is present, the same precautions are to be observed as described under copper.

The ferrocyanide of zinc which is mixed with ferric oxide, preserves its naturally white colour as long as the liquid yet contains free zinc, but its colour changes to a greyish white as soon as a very slight excess of the ferrocyanide solution is present; the liquid then also becomes turbid, and the precipitate settles very slowly. By these constantly-occurring and quite characteristic signs, the end of the operation may be always recognised. In order to make sure, the liquid should be stirred up with a glass rod which has been just previously moistened with an acidified and dilute solution of ammoniacal cupric nitrate, which will have the effect of indicating any excess of the ferrocyanide solution, by exhibiting the more or less intense colour characteristic of cupric ferrocyanide. The zinc solution should be at a temperature of from 40° to 50°, whereby the rapid precipitation and subsidence of the ferrocyanide of zinc is promoted.

When filtration is avoided, the presence of the gelatinous silica (due to the decomposition of silicates of zinc occurring in the ores of that metal, and brought to a gelatinous condition by the treatment of such ores with hydrochloric acid) does not interfere with the correctness and good results of this method of estimating zinc quantitatively in its ores.

MANGANIC PEROXIDE.

§ 53. 2 atoms ferrous oxide are changed to the ferric state by 1 atom of manganic peroxide, therefore $112 \text{ Fe} = 87 \text{ MnO}^2$. 1 atom oxalic acid is decomposed by 1 atom manganic peroxide, therefore $126 \text{ O} = 87 \text{ MnO}^2$. For systematic calculation, however, monobasic numbers are taken, 56 Fe or $63 \text{ O} = 43.5 \text{ MnO}^2$.

Factors.

Metallic iron	×	0.7768 = MnO^2
Cryst. oxalic acid	×	0.6916 = ditto.
Double iron salt	×	0.111 = ditto.

1 c.c. $\frac{N}{16}$ permanganate, bichromate, or hyposulphite = 0.00435 gm. manganic peroxide.

The ores of manganese contain the metal in various states of oxidation, but as they are valued solely by the amount of available oxygen which they contain, it is invariably calculated as peroxide; therefore the above factors all apply to that substance.

Factors for the other oxides can be found readily if required.

All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid yield chlorine equivalent to the oxygen contained in them above the first stage of oxidation. The chlorine so produced can be allowed to react upon a known weight of ferrous salt, and when the reaction is complete, the unchanged amount of iron salt is found by permanganate or bichromate.

Or, the reaction may take place with oxalic acid, resulting in the production of carbonic acid, which can be weighed as in Fresenius and Wills' method, or the amount of unchanged acid remaining after the action can be found by permanganate.

Or again, the chlorine so evolved may be led by a suitable arrangement into a solution of potassic iodide, there setting free an equivalent quantity of iodine, which is found by the aid of sodic hyposulphite.

There are several other methods of analysing the oxides of manganese, but as we have to do with the volumetric processes only, and with the best of them, the three here mentioned will be given in detail.

1. Technical Examination of Manganese Ores, Pyrolusite, Braunite, Manganite, Psilomelane, &c.

One of the most important things connected with the analysis of Manganese ores is the determination of moisture; and as disputes arise sometimes between analysts and those who buy and sell, simply because the sample examined by one analyst contained more or less moisture than one from the same bulk examined by another, it is always best to mention the amount of moisture found in the sample upon the certificate of analysis. Fresenius has found by a most careful series of experiments that the temperature at which all hygroscopic moisture is expelled, without disturbing that which is chemically combined, is 120°C , and this temperature is now used by most English and continental chemists. The drying apparatus devised by Fresenius consists of a round cast-iron air chamber, about ten inches in diameter and two inches deep, having six openings at the top, into which little brass pans, two and a half inches diameter, are dropped, containing the very finely powdered ore; into one of the pans the bulb of a thermometer is placed, imbedded in iron filings, and the instrument kept upright by an iron rod and ring attached to the upper surface of the air chamber; the whole is supported by a tripod, and heated by a gas flame to the required temperature.

As only those who are continually analysing manganese ores would require a drying apparatus of this kind, a simpler contrivance is desirable for occasional use, and this is best managed by a common iron ladle: it can be supported upon a retort ring, and heated by a gas or spirit lamp, using a tube thermometer for stirring the powder, and keeping it at a temperature of about 115°C for about an hour, and lastly raising it to 120° , keeping it constantly stirred; then remove the heat, empty the powder into a porcelain crucible or dish, and let it cool somewhat under the exsiccator; before it is quite cold transfer to a small stoppered and accurately weighed bottle. The ore, when powdered and dried at this temperature, rapidly absorbs moisture on exposing it to the air, and consequently if a definite quantity has to be weighed it must be done quickly; therefore it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which with its contents and stopper is accurately known; about 1 or 2 gm. or any other quantity within a trifle can be emptied into the proper

vessel for analysis, and the exact quantity found by re-weighing the bottle after the stopper is inserted.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to insure its complete and rapid decomposition by the hydrochloric acid.

Considerable discussion has arisen of late as to the best processes for estimating the available oxygen in manganese ores, arising from the fact that many of the ores now occurring in the market contain iron in the ferrous state, and if such ores are analysed by the usual iron method with hydrochloric acid, a portion of the chlorine produced is employed in oxidising the iron contained in the original ore. Such ores, if examined by Fresenius and Wills' method, show therefore a higher percentage than by the iron method, since no such consumption of chlorine occurs in the former process. Manufacturers have therefore refused to accept certificates of analysis of such ores when based on Fresenius and Wills' method. This renders the volumetric processes of more importance, and hence various experiments have been made to ascertain their possible sources of error.

The results show that, with certain modifications, the three enumerated above give very satisfactory results. (See Scherer and Rumpf, "Chem. News," vol. xx. p. 302; also Pattinson, *ibid.*, vol. xxi. p. 266; and Paul, vol. xxi. p. 16.)

2. Direct Analysis by Distillation with Hydrochloric Acid, and Titrating with Sodid Hyposulphite.

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of Manganese or mixtures of them; it also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and, further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The apparatus necessary for the operation is shown in fig. 23, or, instead of this, the arrangement devised by Fresenius or Bunsen may be used. For precautions in conducting the distillation, see § 32.

In order that the percentage of peroxide shall be directly expressed by the number of c.c. or dm. of $\frac{N}{10}$ hypsulphite solution used, 0.436 gm. or 4.36 grn. of the properly dried and powdered

sample is weighed and put into the little flask ; solution of potassic iodide, in sufficient quantity to absorb all the iodine set free, is put into the large tube (if the solution containing $\frac{1}{10}$ at. or 33.2 gm. in the litre is used about 70 or 80 c.c. or dm. will in ordinary cases be sufficient) ; hydrochloric acid is then poured into the distilling flask, and the operation conducted as in § 32.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample bottle into the flask, and find the exact weight afterwards. The titration proceeds as in § 31.4.

3. Determination by Oxalic Acid.

The very finely powdered ore is brought in contact with a known volume of normal oxalic acid, sulphuric acid added, and the mixture heated and well shaken to bring the materials in contact and liberate the carbonic acid ; when the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume, say 300 c.c. and 100 c.c. of the dirty milky fluid, well acidified, diluted, and titrated for the excess of oxalic acid by permanganate ; if, in consequence of the impurities of the ore, the mixture is brown or reddish coloured, this would of course interfere with the reaction of the permanganate, and consequently the mixture in this case must be filtered ; the 300 c.c. are therefore well shaken and poured upon a large and good filter ; when about 100 c.c. have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution is not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of its well-known bright rose-red ; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4.357 gm. of the ore be weighed for analysis, the number of c.c. of normal oxalic acid will be the percentage of peroxide ; but as that is rather a large quantity, and takes some time to dissolve and decompose, half the quantity may be taken, when the percentage is obtained by doubling the c.c. of oxalic acid.

Example : The permanganate was titrated with normal oxalic acid and found that 10 c.c. = 2.5 c.c. normal oxalic, therefore, 1 c.c. = 0.25 c.c. normal oxalic. 2.178 gm. of a fine sample of commercial manganese (Pyrolusite) was treated with 50 c.c. of normal

oxalic acid, together with 5 c.c. of concentrated sulphuric acid until the decomposition was complete; the resulting solution was milky, but contained nothing to hinder the colour of the permanganate, and, therefore, needed no filtration; it was diluted to 300 c.c. and 100 taken for titration, and required 6.2 c.c. permanganate; a second 100 c.c. required 6.3, mean 6.25, which multiplied by 3 gave 18.75 c.c.; this multiplied by the factor 0.25 to convert it into oxalic acid, gave 4.68 c.c. normal oxalic, and this being deducted from the original 50 c.c. used, left 45.32 c.c. = 90.64% pure manganic oxide.

This process possesses an advantage over the following, inasmuch as there is no fear of false results occurring from the presence of air; the analysis may be broken off at any stage, and taken up at the operator's convenience.

4. Determination by Iron.

The most satisfactory form of iron to be used in this process is thin annealed iron wire, which is extremely pure, and readily soluble in sulphuric acid; if a perfectly dry and unoxidised double iron salt is at hand, its use saves time; 1 atom of this salt = 392, represents 43.5 of manganic peroxide, consequently, 1 gm. pure peroxide requires 9 gm. double salt; or in order that the percentage shall be obtained without calculation 1.111 gm. ore may be weighed and digested in the presence of free sulphuric acid, with 10 gm. of double salt, the whole of which would be required supposing the sample was pure peroxide. The undecomposed iron salt remaining at the end of the reaction is estimated by potassic permanganate or bichromate; the quantity so found is deducted from the original 10 gm., and if the remainder be multiplied by 10 the percentage of oxide is gained.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of double salt, the weight of which is known; after the undecomposed quantity is found by permanganate or bichromate, the remainder is multiplied by the factor, 0.111, which gives the proportion of pure peroxide present, whence the percentage may be calculated.

The decomposition of the ore may very conveniently be made in the flask apparatus, fig. 26. The ore is first put into the decomposing flask, then the iron salt and water, so as to dissolve the salt to some extent before the sulphuric acid is added. Sulphuric acid should be used in considerable excess, and the flask heated by the

spirit lamp till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate or bichromate. Instead of this apparatus, a single flask, with bent tube dipping under water, will be equally convenient.

Example: 1 gm. of double iron salt was titrated with permanganate solution, of which 21.4 c.c. were required.

A portion of the prepared ore was shaken out of the sample bottle, and found to weigh 1.24 gm.; 10 gm. of double salt, with a little water, was added (where many manganese analyses are made, it is convenient to keep the required quantity weighed in homœopathic tubes well corked), and sulphuric acid poured in; after the decomposition was complete, 32.5 c.c. of permanganate were required to titrate the undecomposed iron salt; consequently

$$21.4 : 1 :: 32.5 : 1.51.$$

1.51 gm., therefore, being deducted from 10 gm., left 8.49 gm., which multiplied by 0.111, gave 0.942 gm. pure peroxide, whence the percentage is as follows—

$$1.24 : 0.942 . 100 : x = 75.9\%.$$

1.111 gm. of the same sample was accurately weighed and digested with 8 gm. iron salt, and sulphuric acid as before; after the decomposition 8.8 c.c. of permanganate were required to peroxidise the undecomposed iron salt = 0.42 gm., which deducted from the 8 gm. originally used, left 7.58 gm.; or placing the decimal point one place to the right, 75.8% pure manganic peroxide.

In the last example, 8 gm. of iron salt were used, because from the former experiment the percentage of the ore was known, and therefore did not need to exceed the required quantity to any extent. It is always advisable to do this, where possible, as there is then less chance of error from the presence of air; as most samples do not exceed 80 per cent., 8 gm. is sufficient.

In the case of using $\frac{N}{10}$ bichromate for the titration, the following plan is convenient: 100 c.c. or dm. $\frac{N}{10}$ bichromate = 4.032 gm. or 40.32 grn. double iron salt; therefore if 0.436 gm. or 4.36 grn. of the sample of ore is boiled with 4.032 gm. or 40.32 grn. of the double salt and acid, the number of c.c. or dm. of bichromate required will be the percentage.

Example: 4.36 grn. of the same sample as examined before, was boiled with 40.32 grn. double salt, and afterward required 24 dm. of $\frac{N}{10}$ bichromate, which deducted from 100, leaves 76% oxide, agreeing very closely with the previous examinations.

In the case of using metallic iron for the titration (which in most cases is desirable), Pattinson proceeds as follows:—30 grs. of clean iron wire are placed in a 20 oz. flask, with three oz. of dilute sulphuric acid, made by adding 3 parts of water to 1 of oil of vitriol.* A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 30 grs. of the finely pounded and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 8 or 10 oz. with distilled water. The amount of iron remaining unoxidised in the solution is then ascertained by means of a standard solution of potassic bichromate. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been peroxidised by the manganese ore, and from which can be calculated the percentage of manganic peroxide contained in the ore. Thus, supposing it were found that 4 gr. of iron remained unoxidised, then $30 - 4 = 26$ gr. of iron which have been oxidised by the 30 grs. of ore. Then, as

$$\begin{array}{cccc} \text{Fe} & \text{MnO}^2 & \text{Fe} & \text{MnO}^2 \\ 56 & : 43\cdot5 & : & 26 : 20\cdot2. \end{array}$$

the amount of peroxide in the 30 grs. of ore. The percentage is, therefore, 67·33. Thus—

$$30 : 20\cdot2 = 100 : 67\cdot33$$

grain weights are given in this example, but those who use the gramme system will have no difficulty in arranging the details accordingly.

MANGANOUS OXIDE.

$$\text{MnO} = 71.$$

Factor for $\frac{N}{16}$ permanganate, 0·00355 gm., or 0·0355 grn.

Potassic ferrocyanide \times 0·0842 = MnO

Double iron salt \times 0·0911 = „

* Pattinson has proved, what has long been evident to myself, that the oxidation of iron dissolved in sulphuric acid is far less active than in hydrochloric.

§ 54. If protoxide or a protosalt of manganese is boiled with an alkaline solution of red prussiate of potash, the latter becomes converted into ferrocyanide, while the manganese precipitates as hydrated peroxide. Lenssen found, however, that the composition of the precipitate was not uniform; that is to say, its state of oxidation, unless at least 1 eq. of ferric oxide was added with every eq. of manganese. The precipitate, under these circumstances, possesses a constant composition. The amount of manganese present is indirectly found by titrating the resulting ferrocyanide of potassium with permanganate, 2 eq. of which = 1 eq. MnO .

The results are very satisfactory with certain precautions suggested by Fresenius, namely:—

1. That the solution of caustic potash or soda used must be free from organic matter; if pure solid alkalies are used, they should be fused in a silver crucible before being added.

2. That the boiling must not be continued too long, for if pure potash and ferridecyanide are boiled for some considerable time, traces of ferrocyanide are produced.

3. The precipitate must be exceedingly well washed; and being rather voluminous, this occupies some time.

The Analytical Process.

The acid solution of manganous oxide is mixed with a solution of ferric chloride, in such proportion that not less than 1 eq. Fe^2O^3 is present with every eq. of MnO . The mixture is then added, little by little, to a boiling alkaline solution of potassic ferridecyanide; after a few minutes boiling, the precipitate becomes granular, and shrinks somewhat. The flask is then put aside till *quite* cold (the hot solution would be affected by the reducing action of the filter), then filtered and thoroughly washed; the filtrate, or a portion of it, titrated, after acidifying with sulphuric acid and warming, with permanganate.

A shorter but somewhat less exact method is to dilute the mixture after boiling, to a definite volume, say 300 c.c.; allow to settle thoroughly; then take out 100 c.c. or so for titration. The bulky precipitate interferes, to a small extent, with the accurate measurement of the liquid; and this difficulty is increased when a great excess of oxide of iron is present. A mean of five determinations made by Fresenius on this plan, using only a slight excess of iron, gave 99.12 instead of 100; therefore quite satisfactory for cases where the greatest accuracy is not required.

TIN.

$$\text{Sn} = 118.$$

Metallic iron	×	1.0536	= Tin.
Double iron salt	×	0.1505	= „
Factor for $\frac{N}{10}$ iodine or permanganate solution		0.0059	

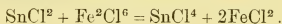
§ 55. THE method originally devised by Streng for the direct estimation of tin by potassic bichromate, or other oxidising agents in acid solution, has been found most unsatisfactory, from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride, there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, and which are found satisfactory.

1. Direct Titration by Iodine in Alkaline Solution (Lenssen).

Metallic tin or its protosalt is dissolved in hydrochloric acid, if not already in solution, a tolerable quantity of the double tartrate of soda and potash added, together with sodic bicarbonate in excess. If enough tartrate is present, the solution will be clear; starch liquor is then added, and the mixture titrated with $\frac{N}{10}$ iodine, till the blue colour is permanent; metallic tin is best dissolved in hydrochloric acid by placing a platinum crucible or cover in contact with it so as to form a galvanic circuit.

2. Indirect Titration by Ferric Chloride and Permanganate (Löwenthal, Stromeyer, &c.)

This method owes its value to the fact that when stannous chloride is brought into contact with ferric or cupric chloride, it acts as a reducing agent, in the most exact manner, upon these compounds, stannic chloride being formed, together with a proportionate quantity of ferrous or cuprous salt, as the case may be; if either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron;—



56 iron = 59 tin. If decinormal permanganate, or the factor necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

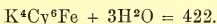
The solution of protochloride, or other protosalt of tin in hydrochloric acid, or the granulated metal, is mixed with pure ferric chloride, which if tolerably concentrated, dissolves metallic tin readily, and without evolution of hydrogen, diluted with distilled water, and titrated with permanganate as usual; to obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which ferric chloride is added; the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Stannic salts, also tin compounds containing iron, are dissolved in water, hydrochloric acid added, and a plate of clean zinc introduced for ten or twelve hours; the tin so precipitated is carefully collected and washed, then dissolved in hydrochloric acid, and titrated as above; or the finely divided metal may at once be mixed with an excess of ferric chloride, a little hydrochloric acid added, and when solution is complete, titrated with permanganate; 4 at. iron (= 224) occurring in the form of protochloride, represent 1 at. (= 118) tin.

Tin may also be precipitated from slightly acid peroxide solution, as sulphide, by sulphuretted hydrogen gas or water, the sulphide well washed, and mixed with ferric chloride; the mixture gently warmed, and the sulphur filtered off; the filtrate then titrated with permanganate as above, 4 at. iron = 1 at. tin.

YELLOW AND RED POTASSIC PRUSSIATES.

Potassic Ferrocyanide.



Metallic iron	×	7.541	= Crystallised potassic ferrocyanide.
Double iron salt	×	1.077	= " " "

1. De Haen's Method.

§ 56. THIS substance may be estimated by potassic permanganate, which acts by converting it into red prussiate. The process is easy of application, and the results accurate. De Haen recommends that a standard solution of pure ferrocyanide should be

used as the basis upon which to work, and this is advisable ; it can, however, be dispensed with, if the operator chooses to calculate the strength of his permanganate upon iron or its compounds. If the permanganate is decinormal, there is of course very little need for calculation (1 at. = 422 must be used as the systematic number, and therefore 1 c.c. of $\frac{N}{10}$ permanganate is equal to 0.0422 gm. of yellow prussiate). The standard solution of pure ferrocyanide contains 20 gm. in the litre ; each c.c. will contain 0.020 gm.

The Analytical Process.

10 c.c. of the standard prussiate solution are put into a white porcelain dish or beaker standing on white paper, and 250 c.c. or so of water added ; it is then acidified pretty strongly with sulphuric acid, and the permanganate delivered from the burette until the pure yellow colour disappears, and gives place to a beautiful uranium yellow colour ; it is then cautiously added until the faintest pink tinge occurs. De Haen, Fresenius, and Mohr all agree in stating that the end of the reaction is hindered by turbidity ; this I have not found to be the case, but have invariably found that when the solution of ferrocyanide is very dilute, say $\frac{1}{2}$ gm. to 10 or 12 oz. water freely acidified, and the operation performed in a clean white evaporating basin, that the mixture remains clear, and the end is very exactly shown ; a drop or two in excess of permanganate being sufficient to give the necessary pinkish tinge. I attribute the different experience obtained by us to the fact, that I invariably use pure permanganate of potash for titration, and sulphuric instead of hydrochloric acid.

Potassic ferrocyanide may be estimated, when mixed with sulphocyanide, by standard solution of cupric sulphate, the whole of the ferrocyanogen being carried down in combination with the copper ; the ending of the titration may be found by bringing a drop of the liquid in contact with a drop of ferric chloride on filter paper. If alkaline sulphides are present, the solution should be boiled with lead carbonate, filtered, acidified with sulphuric acid, then titrated with the copper solution.

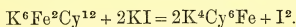
POTASSIC FERRIDCYANIDE.



Metallic iron	$\times 5.88$	= Potassic ferridcyanide.
Double iron salt	$\times 1.68$	= " "
$\frac{N}{10}$ Hyposulphite	$\times 0.0329$	= " "

1. Lenssen's Method.

§ 57. THIS salt can be estimated either by reduction to ferrocyanide and titration with permanganate or bichromate as above, or by Lenssen's method, which is based upon the fact, that when potassic iodide and ferridcyanide are mixed with tolerably concentrated hydrochloric acid, iodine is set free.



the quantity of which can be estimated by $\frac{N}{10}$ hyposulphite and starch liquor; this method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions. C. Mohr's modification (see Zinc, § 50) is, however, more reliable, and is as follows:—The ferridcyanide is dissolved in a convenient quantity of water, potassic iodide in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure zinc sulphate in excess; after standing a few minutes to allow the decomposition to perfect itself, the excess of acid is neutralised by sodic carbonate, so that the latter slightly predominates.

At this stage all the zinc ferridcyanide first formed is converted into the ferrocyanide of that metal, and an equivalent quantity of iodide set free, which can at once be titrated with $\frac{N}{10}$ hyposulphite and starch, and with very great exactness. 1 c.c. $\frac{N}{10}$ hyposulphite = 0.0329 gm. potassic ferridcyanide.

The mean of five determinations made by Mohr gave 100.21 instead of 100.

2. Reduction of Ferrid to Ferrocyanides.

This process is, of course, necessary when the determination by permanganate has to be made, and is best effected by boiling the weighed ferridcyanide with an excess of potash or soda, and adding small quantities of concentrated solution of ferrous sulphate until the precipitate which occurs possesses a blackish colour (signifying that the magnetic oxide is formed); the solution is then diluted to a convenient quantity, say 300 c.c., well mixed and filtered through a dry filter; 50 or 100 c.c. can then be taken, sulphuric acid added, and titrated with permanganate as before described.

Other soluble ferro or ferridcyanides can be examined in the same way as the potassium salts, and if insoluble, they may generally be converted into the latter by boiling with strong caustic potash.

LIME.

$$\text{CaO} = 56.$$

1 c.c. $\frac{N}{10}$ permanganate	= 0.0028 gm. CaO
„ „	= 0.0050 gm. CaCO_3
„ „	= 0.0086 gm. $\text{CaSO}_4 + 2\text{H}_2\text{O}$
„ normal oxalic acid	= 0.0280 gm. CaO
Cryst. oxalic acid $\times 0.444$	= CaO
Double iron salt $\times 0.07143$	= CaO

§ 58. THE estimation of lime alkalimetrically has already been given, but that method is of limited application, unless oxalate of lime, in which form lime is generally separated from other bases, be converted into carbonate or caustic lime by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel, are as exact in their results as the determination of lime by weight; and where a series of estimations have to be made, the plan is very convenient—

1. The lime is precipitated by ammoniacal oxalate from an ammoniacal or acetic acid solution, the precipitate well washed, then together with the filter, pushed through the funnel into a large flask, acidified, and diluted freely; then titrated with permanganate, as described in § 27.4.

$$63 \overline{\text{O}} = 28 \text{ CaO}.$$

2. Is applicable in certain cases only, but saves time when it can be applied. To the lime solution (which must contain no substance capable of decomposing permanganate) a measured excess of normal oxalic acid is added; the precipitated oxalate of lime allowed to settle in a 300 c.c. flask, and 100 c.c. of the clear liquid acidified and titrated for the excess of oxalic acid; the quantity so found is multiplied by 3, deducted from that originally added, and the remainder multiplied by the factor for normal oxalic acid.

LEAD.

$$\text{Pb.} = 207.$$

1 c.c. $\frac{N}{10}$ permanganate	= 0.01035 gm. Lead.
1 c.c. normal oxalic acid	= 0.1035 gm. „
Metallic iron \times	1.848 = Lead
Double iron salt \times	0.264 = „
Crystallised oxalic acid \times	1.643 = „

§ 59. THE estimation of lead is in most cases more securely effected by weight than by measure ; there are, however, instances in which the latter process may be used with advantage, and consequently the following methods are given :—

1. Hempel's Method (modified).

The lead solution, which must contain no other body precipitable by oxalic acid, is put into a 300 c.c. or dm. flask, and a measured quantity of normal oxalic acid added in excess, ammonia is then added to slight predominance, the flask filled to the mark with water shaken, and put aside to settle ; 100 c.c. or dm. of the clear liquid may then be taken, acidified with sulphuric acid, and titrated for the excess of oxalic acid with permanganate ; the amount so found multiplied by 3, and deducted from that originally added, will give the quantity combined with the lead.

Where the nature of the filtrate is such that permanganate cannot be used for titration, the precipitate must be collected, well washed, dissolved in dilute nitric acid, sulphuric acid added, and titrated with permanganate.

In neither case are the results absolutely accurate, owing to the slight solubility of the precipitate, but with careful manipulation the error need not exceed 1 per cent.

2. Schwarz's Method.

The lead is precipitated as chromate, well washed and digested with a weighed excess of double iron salt and hydrochloric acid ; the result is ferric and chromic chloride, together with lead chloride, and undecomposed iron salt. The quantity of the latter is found, after filtering off the lead chloride, by permanganate, and deducted from the original weight ; the remainder, multiplied by the factor 0.264, will give the weight of lead.

Schwarz has simplified this method as follows :—The standard solution being 14.73 gm. pure potassic bichromate in a litre of water, 1 c.c. of this solution precipitates 0.0207 gm. lead.

In the analysis of metallic lead, a certain quantity of it should be dissolved in its minimum of nitric acid, the solution diluted with water, carefully neutralised with ammonia or sodic carbonate, and excess of sodic acetate added, and the solution precipitated by the bichromate solution. When the precipitation approaches its end, or when the precipitate commences readily to subside, some drops of a neutral solution of nitrate of silver are deposited on a porcelain

plate, and the bichromate solution only added by two or three drops at a time to the liquid under examination ; after each addition the whole is well stirred, allowed to subside, and a drop of the clear liquor added to one of the drops of the silver solution. As soon as the bichromate is in excess the two drops form a red colour, while the precipitated chromate of lead has no effect on the silver test, but simply floats on the top as a yellow precipitate. Should the solution assume a yellow colour before the silver reaction has commenced, it would indicate that not sufficient acetate of soda had been added in the first instance, and it would be necessary to add this now, and also a cubic centimetre of a normal lead solution, containing 0.0207 of lead as nitrate. The slight turbidity which first takes place soon goes off, and the operation may be proceeded with as before. One cubic centimetre must naturally, in such instance, be deducted from the amount of chrome solution, on account of the extra addition of lead. Experiments made with 0.6975 grammes of the purest lead of Tarnowitz gave the following results :—It required 33.7 of bichromate solution, as it is always necessary to have a slight excess of bichromate, we may assume that 33.6 cubic centimetres were only requisite for the precipitation of the lead. $33.6 \text{ multiplied by } 0.0207 = 0.6955 \text{ grammes, or } = 99.72 \text{ per cent.}$, showing that it was nearly pure lead.

0.399 gm. of well-dried nitrate of lead required also one 12.0 of bichromate indicating 0.2484 gm. of lead, or 62.29 per cent. According to calculation, nitrate of lead should contain 62.54 per cent.

0.385 gm. of crystallised acetate of lead required 10.2 of chrome solution = to 0.211 gm., or 54.84 per cent. of lead, while according to the formula $\text{Pb}_2\text{A} + \text{H}_2\text{O}$, it should have been 54.61 per cent.

Copper, cadmium, zinc, ferric salts, and cobalt, do not interfere with the reaction—but all metals precipitable by chromic acid should of course be removed.

3. Mohr's Alkalimetric Method (results tolerably accurate).

The lead is precipitated as carbonate by means of a slight excess of ammoniac carbonate, together with free ammonia, the precipitate well washed, and dissolved in a measured excess of normal nitric acid ; neutral solution of sodic sulphate is then added to precipitate the lead as sulphate ; without filtering, the excess of nitric acid is then estimated by normal alkali, each c.c. or dm. combined being equal to 0.1035 gm. or 1.035 grn. lead.

ASSAY OF REFINED METALLIC LEAD.

§ 60. Fresenius has published an extensive memoir (Zeitschrift, vol. viii. p. 148) on the estimation of the small quantities of other metals occurring in refined lead, and which have undoubtedly a considerable effect upon its value for many purposes, such as chambers for sulphuric acid manufacture, &c. The refining process is carried on generally now so well that refined soft lead can commonly be obtained containing from 99.94 to even 99.995% pure lead. The metals generally found as impurities are silver, copper, antimony, bismuth, cadmium, zinc, iron, and nickel, with traces of cobalt, manganese, and arsenic. Of these the most commonly found are silver, iron, antimony, copper, and zinc, all of which, according to Fresenius' experiments, may be estimated volumetrically with greater exactness than by weight. The process of separation are fully described in the memoir alluded to, but as it is too lengthy for insertion here, those who desire to carry out the process are referred to the original article.

MERCURY.

Hg = 200.

Factor for $\frac{N}{10}$ solutions of permanganate, iodine,

or salt

0.0200 gm. Hg

0.0208 „ HgO

0.0271 „ HgCl²

Double iron salt × 0.5104 = Hg

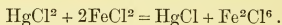
„ „ × 0.6914 = HgCl².

1. **Precipitation as Mercurous Chloride by $\frac{N}{10}$ Salt Solution, and estimation of the excess of Salt by $\frac{N}{10}$ Silver and Potassic Chromate (results accurate).**

§ 61. THE solution to be titrated must not be warmed, and contain the metal only in the form of protoxide. The salt solution is added in slight excess, the precipitate washed with the least possible quantity of water to ensure the removal of all the salt; to the filtrate a few drops of chromate solution are added, then pure sodic carbonate till the liquid is of clear yellow colour, $\frac{N}{10}$ silver is then delivered in till the red colour occurs. The quantity of salt so found is deducted from that originally used, and the difference calculated in the usual way.

2. Mohr's Method.

This process is based on the fact that when mercuric chloride (sublimite) is brought in contact with an alkaline solution of ferrous oxide in excess, the latter is converted into ferric oxide while the mercury is reduced to mercurous chloride (calomel), the excess of ferrous oxide is then found by permanganate or bichromate—



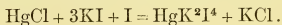
It is therefore advisable in all cases to convert the mercury to be estimated into the form of sublimate, secured by evaporating it to dryness with nitro-hydrochloric acid; this must take place, however, below boiling heat, as vapours of chloride escape with steam at 100° (Fresenius.)

Nitric acid or free chlorine must be altogether absent during the decomposition with the iron protosalt, otherwise the residual titration will be inexact, and the quantity of the iron salt must be more than sufficient to absorb half the chlorine in the sublimate.

Example: 1 gm. pure sublimate was dissolved in warm water and 3 gm. double iron salt added, then solution of caustic soda till freely alkaline. The mixture became muddy and dark in colour, and was well shaken for a few minutes, then sodic chloride and sulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of ferric oxide dissolved, leaving the calomel white; it was then diluted to 300 c.c., filtered through a dry filter, and 100 c.c. titrated with $\frac{N}{10}$ permanganate, of which 13.2 c.c. were required—multiplied by 3 = 39.6, which deducted from 76.5 c.c. (the quantity required for 3 gm. double iron salt), left 36.9 c.c. = 1.446 gm. undecomposed iron salt, which multiplied by the factor 0.6914, gave 0.999 gm. sublimate, instead of 1 gm., or the 36.9 c.c. may be multiplied by the $\frac{N}{10}$ factor for mercuric chloride, which will give the same figures exactly.

3. Hempel's Method (results accurate).

If the mercury exists as a protosalt it is precipitated by sodic chloride, the precipitate well washed, and together with its filter pushed through the funnel into a stoppered flask, a sufficient quantity of potassic iodide added, together with $\frac{N}{10}$ iodine solution (to 1 gm. calomel about 2.5 gm. of iodide, and 100 c.c. $\frac{N}{10}$ iodine), the flask closed, and shaken till the precipitate has dissolved—



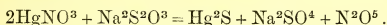
The brown solution is then titrated with $\frac{N}{10}$ hyposulphite till colourless, then diluted to a definite volume, and a measured portion titrated with $\frac{N}{10}$ iodine and starch for the excess of hyposulphite—
1 c.c. $\frac{N}{10}$ iodine = 0.02 gm. Hg.

Where the mercurial solution contains nitric acid, or the metal exists as peroxide, it may be converted into protochloride by the reducing action of ferrous sulphate, as in Mohr's method. The solution must contain hydrochloric acid or common salt in sufficient quantity to transform all the mercury into calomel. At least three times the weight of mercury present of ferrous sulphate in solution is to be added, then caustic soda in excess, the muddy liquid well shaken for a few minutes, then dilute sulphuric acid added in excess, and the mixture stirred till the dark coloured precipitate has become perfectly white. The calomel so obtained is collected on a filter, well washed, and titrated with $\frac{N}{10}$ iodine and hyposulphite as above.

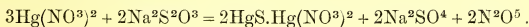
4. Direct Titration with Sodid Hyposulphite (Scherer), results accurate in the absence of other metals precipitable by hyposulphite.

The solution of hyposulphite is in all cases made by dissolving $\frac{1}{20}$ eq. = 12.4 gm. of the salt in 1 litre of water, or by mixing equal volumes of $\frac{N}{10}$ hyposulphite and distilled water.

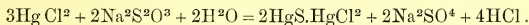
The reaction which takes place with hyposulphite in the case of mercurous nitrate is



With mercuric nitrate—



With mercuric chloride—



a. Mercurous Salts.

The solution containing the metal only as a protosalt is diluted, gently heated, and the hyposulphite delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown colour. The sulphide settles freely, and allows the end of the reaction to be easily seen. 1 c.c. of hyposulphite solution is equal to 0.020 Hg., or 0.0208 Hg²O.

b. Mercuric Nitrate.

The solution is considerably diluted, put into a stoppered flask, nitric acid added, and the hyposulphite cautiously delivered from the burette, vigorously shaken meanwhile until the last drop produces no further yellow precipitate. Scherer recommends that when the greater part of the metal is precipitated, the mixture should be diluted to a definite volume, the precipitate allowed to settle, and a measured quantity of the clear liquid taken for the completion of the process; the analysis may then be checked by a second titration of the clear liquid, if needful. 1 c.c. hyposulphite is equal to 0.015 Hg., or 0.0162 HgO.

c. Mercuric Chloride.

With mercuric chloride (sublimate) the end of the process is not so easily seen; the course of procedure is as follows:—The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the hyposulphite cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty looking colour. Filtration is necessary to distinguish the exact ending of the reaction, for which purpose Dr Beale's filter, fig. 25, is useful.

Liebig's method is the reverse of that used for determining chlorides in urine, § 77.2 *b*, sodic phosphate being used in the estimation of mercury, as indicator, instead of the urea occurring naturally in the urine. The method is capable of very slight application. For details, see § 77. 4.

5. Estimation as Mercuric Chloride by Potassic Iodide. Personne (Comptes Rendus lvi. 63).

This process is founded on the fact that if a solution of mercuric chloride be added to one of potassic iodide, in the proportion of 1 atom of the former to 4 of the latter, red mercuric iodide is formed, which dissolves to a colourless solution until the balance is overstepped, when the brilliant red colour of the iodide appears as a precipitate, which, even in the smallest quantity, communicates its tint to the liquid. The mercuric solution must always be added to the potassic iodide; a reversal of the process—though giving eventually the same quantitative reaction, is nevertheless much less speedy and dependable. The mercurial compounds to be estimated by this process must invariably be brought into the form of neutral mercuric chloride.

The standard solutions required are decinormal, made as follows:—

Solution of potassic iodide: 33·2 gm. pure salt is dissolved, and diluted to 1 litre—1 c.c. = 0·01 gm. Hg., or 0·01355 gm. HgCl_2 .

Solution of mercuric chloride: 13·55 gm. of the salt, with about 30 gm. pure sodic chloride (to assist the solution of the mercuric salt), are dissolved and diluted to 1 litre, 1 c.c. = 0·1 gm. Hg.

The conversion of various forms of mercury into mercuric chloride is, according to Personne, best effected by heating with caustic soda or potash, and passing chlorine gas into the mixture, which is afterwards boiled to expel excess of chlorine (the mercuric chloride is not volatile at boiling temperature when associated with alkaline chloride); the solution is then cooled and diluted to a given volume, placed in a burette, and delivered into a measured volume of the decinormal potassic iodide until the characteristic colour occurs; it is preferable to dilute the mercuric solution considerably, and make up to a given measure, say 300 or 500 c.c.—and as a preliminary trial take 20 c.c. or so of potassic iodide solution, and titrate it with the mercuric solution approximately with a graduated pipette, the exact strength may then be found by using a burette of sufficient size.

GOLD.

$$\text{Au} = 196\cdot5.$$

1 c.c. or 1 dm. normal oxalic acid = 0·0655 gm. or 0·655 grn. gold.

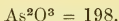
§ 62. THE technical assay of gold for coining purposes is invariably performed by cupellation. Terechloride of gold is, however, largely used in photography, and, therefore, it may be necessary sometimes to ascertain the strength of a solution of the chloride or its value as it occurs in commerce.

If to a solution of gold in the form of chloride (free from nitric acid), an excess of oxalic acid be added, in the course of from 18 to 24 hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate, the measure of gold will be obtained.

Example: A 15 grain bottle of the chloride of gold of commerce was dissolved in water, and the solution made up to 300 decems. 20 dm. of normal oxalic acid were then added, and the flask set aside for twenty-four hours in a warm place, at the end of that time

the gold had settled, and the supernatant liquid was clear and colourless. 100 dm. were taken out with a pipette, and titrated with $\frac{N}{10}$ permanganate, of which 25 dm. were required; this multiplied by 3 gives 75 dm. = 7.5 dm. normal oxalic acid, which deducted from the 20 dm. originally added, left 12.5 dm.; this multiplied by $\frac{1}{3}$ rd the equivalent of gold (1 eq. chloride of gold decomposing 3 eq. oxalic acid) = 0.655 gave 8.195 grn. metallic gold, or multiplied by 101 ($=\frac{1}{3}$ eq. chl. gold) gave 12.625 grn.; either way the result was 84 per cent. of chloride of gold instead of 100.

ARSENIOUS ANHYDRIDE.



1. Oxidation by Iodine (Mohr, results accurate).

§ 63. THE principle upon which the determination of this substance by iodine is based is explained in § 33.

It therefore only remains to say, that in the estimation of arsenious compounds by the method there described, it is advisable to use sodic bicarbonate for rendering the solution alkaline in preference to the neutral carbonate, as there is less chance of the iodine being affected by the bicarbonate than by the neutral salt.

To a neutral or watery solution, therefore, it is best to add about 20 or 25 c.c. of saturated solution of pure bicarbonate to every 0.1 gm. or so of As_2O_3 , and then titrate with $\frac{N}{10}$ iodine and starch. When the solution is acid, the excess may be removed by neutral sodic carbonate, then the necessary quantity of bicarbonate added, and the titration completed as before.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = 0.00495 \text{ gm. } \text{As}_2\text{O}_3.$$

2. Oxidation by Potassic Bichromate.

The arsenious compound is mixed with $\frac{N}{10}$ bichromate in excess in presence of hydrochloric acid and water, in such proportion that at least $\frac{1}{6}$ th of the total volume consists of hydrochloric acid, sp. gr. 1.12.

The excess of bichromate is found by a solution of double iron salt, which may be prepared when wanted by weighing a definite quantity and dissolving in water, or the value of the solution may quickly be found by titration with the $\frac{N}{10}$ bichromate to be used for the arsenic estimation; the quantity of bichromate reduced is, of

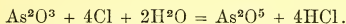
course, the measure of the quantity of arsenious converted into arsenic acid.

$$1 \text{ c.c. } \frac{N}{10} \text{ bichromate} = 0.00495 \text{ gm. As}_2\text{O}_3.$$

3. Indirect Estimation by Distilling with Chromic and Hydrochloric Acids (Bunsen).

The principle of this very exact method depends upon the fact, that when potassic bichromate is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 1 eq. chromic acid. See § 64. 2.

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

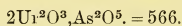


Therefore every 4 eq. of chlorine, short of the quantity yielded when bichromate and hydrochloric acid are distilled alone, represent 1 eq. arsenious acid. The operation is conducted in the apparatus fig. 23, and the titration as in § 31.

4. By Precipitation as Uranic Arsenate (Bödeker, results accurate).

The arsenic must exist in the state of arsenic acid (As_2O_5), and the process is in all respects the same as for the estimation of phosphoric acid, devised by Neubauer, Pincus, and myself, § 72. The strength of the uranium solution may be ascertained and fixed by pure sodic or potassic arsenate, or by means of a weighed quantity of pure arsenious acid converted into arsenic acid by boiling with strong nitric acid. The method of testing is precisely the same as with phosphoric acid, that is to say, the solution of uranium used for P_2O_5 will suffice, and if its exact strength as regards that body be known, a slight calculation will show the quantity to be used for arsenic acid; but it is, nevertheless, preferable to titrate it upon a weighed amount of arsenical compound, bearing in mind here, as in the case of P_2O_5 , that the titration must take place under precisely similar conditions as to quantity of liquid, the amount of sodic acetate and acetic acid added, and the depth of colour obtained by contact of the fluid under titration with the yellow prussiate solution.

The precipitate of uranic arsenate possesses the composition—



CHROMIUM.

Cr = 52·5.

Factors.

Metallic iron	×	0·3123	= Chromium
„	×	0·598	= Chromic acid
„	×	0·8784	= Potassic bichromate
„	×	1·926	= Lead chromate
Double iron salt	×	0·0446	= Chromium
„	×	0·0854	= Chromic acid
„	×	0·1255	= Potassic bichromate
„	×	0·275	= Lead chromate
1 c.c. $\frac{N}{10}$ solution	=	0·003349	gm. CrO^3
„ „	=	0·00492	gm. $\text{K}^2\text{Cr}_2\text{O}^7$

1. Reduction by Iron.

§ 64. THE estimation of chromates is very simply and successfully performed by the aid of ferrous oxide, being the converse of the process devised by Penny for the estimation of iron. See § 30.

The best plan of procedure is as follows. A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular double sulphate of iron and ammonia; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid and small quantities of the iron salt, added from time to time with a dry spoon, taking care that none is spilled, until the mixture becomes green, and the iron is in excess, best known by a small drop being brought in contact with a drop of red prussiate of potash on a white plate; if a blue colour appears at the point of contact, the iron is in excess. It is necessary to estimate this excess, which is most conveniently done by $\frac{N}{10}$ bichromate being added until the blue colour produced by contact with the red prussiate gives place to a yellow brown. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the $\frac{N}{10}$ bichromate deducted from it, and the remainder multiplied by the factor required by the substance sought.

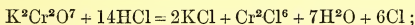
Example: 0·5 gm. pure potassic bichromate was taken for analysis,

and to its acid solution 4.15 gm. double iron salt added. 3.3 c.c. of $\frac{N}{10}$ bichromate were required to oxidise the excess of iron salt; it was found that 0.7 gm. of the salt = 17.85 bichromate solution, consequently 3.3 c.c. of the latter were equal to 0.12985 gm. iron salt; this deducted from the quantity originally used left 4.02015 gm., which multiplied by the factor 0.1255 gave 0.504 gm. instead of 0.5 gm. -

In the case of chromate of lead being estimated in this way, it is best to mix both the chromate and the iron salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before.*

2. Estimation of Chromates by Distillation with Hydrochloric Acid (Bunsen, results very accurate).

When chromates are boiled with an excess of hydrochloric acid in Fresenius', Bunsen's, or Mohr's distilling apparatus, fig. 23, every 1 at. of chromic acid liberates 3 at. chlorine. For instance, with potassic bichromate the reaction may be expressed as follows—



if the liberated chlorine is conducted into a solution of potassic iodide, 3 at. of iodine are set free, and can be estimated by $\frac{N}{10}$ hyposulphite, as in § 31. 3 at. of iodine so obtained = 381, represent 1 eq. chromic acid = 100.50. The same decomposition takes place by mere digestion, as described in § 31. 4.

ANTIMONY.

Sb = 122.

1. Conversion of Antimonious Acid in Alkaline Solution into Antimonic Acid by Iodine (Mohr, results accurate).

§ 65. THE antimonious oxide, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralised by sodic carbonate, then a cold saturated solution of sodic bicarbonate, added in the proportion of 20 c.c. to about 0.1 gm. Sb_2O_3 ; to the clear solution starch liquor and $\frac{N}{10}$ iodine are added until the blue colour appears; the colour disappears after a little time, therefore the first appearance of a permanent blue is accepted as the true measure of iodine required.

1 c.c. $\frac{N}{10}$ iodine = 0.0061 gm. Sb.

* Where pure double iron salt is not at hand, a solution of iron wire in sulphuric acid, freshly made and of ascertained strength, can of course be used.

2. Oxidation by Potassic Permanganate or Bichromate.

Permanganate or bichromate added to a solution of antimonious chloride, containing not less than $\frac{1}{6}$ th of its volume of hydrochloric acid, sp. gr. 1.12, converts it into antimonie chloride.

The reaction is uniform only when the minimum quantity of acid indicated above is present, but it ought not to exceed $\frac{1}{4}$ th the volume, and the precautions before given as to the action of hydrochloric acid on permanganate must be taken into account—hence it is preferable to use bichromate as for arsenic. See § 63. 2.

3. Distillation of Antimonious or Antimonie Sulphide with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen (Schneider, results accurate).

When either of the sulphides of antimony are heated with hydrochloric acid in Bunsen's, Fresenius', or Mohr's distilling apparatus, fig. 23, for every 1 at. of antimony present as sulphide, 3 at. of sulphuretted hydrogen are liberated. If, therefore, the latter be estimated, the quantity of antimony is ascertained. The process is best conducted as follows:—

The antimony to be determined is brought into the form of ter or pentasulphide (if precipitated from a hydrochloric solution, tartaric acid must be previously added, to prevent the precipitate being contaminated with chloride), which, together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The condensing tube, fig. 23, contains a mixture of caustic soda or potash, with a definite quantity of $\frac{N}{10}$ arsenious acid solution, § 33. 1, in sufficient excess to absorb all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, acidified with hydrochloric acid, to precipitate all the arsenious sulphide. The whole is then diluted to, say 300 c.c., and 100 c.c. taken with a pipette, neutralised with sodic carbonate, some bicarbonate added, and the titration for excess of arsenious acid performed with $\frac{N}{10}$ iodine and starch, as directed in § 33.

IODINE.

$$I = 127.$$

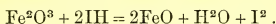
Free and Combined.

1 c.c. $\frac{N}{10}$ hyposulphite	= 0·0127 gm. Iodine
" "	= 0·0166 gm. Potassic iodide

1. By Distillation.

§ 66. FREE iodine is of course very readily estimated by solution in potassic iodide, and titration with starch and $\frac{N}{10}$ hyposulphite, as described in § 32.

Combined iodine, however, in haloid salts, such as the alkaline iodides, must be subjected to distillation with hydrochloric acid, and some other substance capable of assisting in the liberation of free iodine, which is received into a solution of potassic iodide, and then titrated with $\frac{N}{10}$ hyposulphite in the ordinary way. Such a substance presents itself best in the form of ferric oxide, or some of its combinations; if, therefore, hydriodic acid, or what amounts to the same thing, an alkaline iodide, be mixed with an excess of ferric oxide, and distilled in the apparatus shown in fig. 23, the following reaction occurs :—



The best form in which to use the ferric oxide is the double sulphate of peroxide of iron, and ammonia or potash (iron alum).

The iodide and iron alum being brought into the little flask, fig. 23, sulphuric acid, of about 1·3 sp. gr. or so, is added, and the cork carrying the still tube inserted. This tube is not carried into the solution of potassic iodide in this special case, but within a short distance of it, and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube, and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be present in sufficient quantity to absorb it all. When no more violet vapours are to be seen in the flask, the operation is ended; but to make sure, it is well to empty the ioduretted solution of iodine out of the

condensing tube into a beaker, and put a little fresh iodine solution with starch in, then heat the flask again; the slightest traces of iodine may then be discovered by the occurrence of the blue colour. In case this occurs, the distillation is continued a little while, then both liquids mixed, and titrated with $\frac{N}{10}$ hyposulphite as usual.

Ferric chloride may be used instead of the iron alum, but in that case there is some danger of a portion being carried over, which would set iodine free from the iodide, and so give results too high.

The analysis may be checked by titrating the ferrous oxide in the retort with $\frac{N}{10}$ permanganate or bichromate.

2. Estimation of Combined Iodine by Oxidation (Golfier Bessyre and Dupré).

This wonderful sharp method of estimating iodine depends upon its conversion into iodic acid by free chlorine. When a solution of potassic iodide is treated with successive quantities of chlorine water, first iodine is liberated, then chloride of iodine (ICl) formed; if starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue while any of the others will be coloured intense violet; a further addition of chlorine, in sufficient quantity, produces pentachloride of iodine (ICl_5), or rather, as water is present, iodic acid (IO^3H); no coloration of the above substances are produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Bessyre and Dupré, independently of each other for the purpose of estimating iodine. The former suggested the use of starch, the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

The following examples are taken from Mohr:—

30 c.c. of weak chlorine water were put into a beaker with potassic iodide and starch, then titrated with $\frac{N}{100}$ hyposulphite, of which 17 c.c. were required.

10 c.c. of solution of potassic iodide, containing 0.010 gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared; the quantity used was 85.8 c.c. The excess of chlorine was then ascertained by adding sodic bichromate, potassic iodide, and starch; a slight blue colour occurred; this was removed by $\frac{N}{100}$ hyposulphite, of which 1.2 c.c. were used. Now, as 30 c.c. of the chlorine solution required 17 c.c., the 85.8 c.c. required 48.62 c.c. of hypo-

sulphite; from this, however, must be deducted the 1.2 c.c. in excess, leaving 47.42 c.c. $\frac{N}{100} = 4.742$ c.c. of $\frac{N}{10}$ hyposulphite, which multiplied by 0.00211, the one-sixth of $\frac{1}{100000}$ eq. (1 eq. of iodic acid liberating 6 eq. iodine), gave 0.010056 gm. iodine instead of 0.01 gm.

Mohr suggests an improvement upon this method, which dispenses with the use of chloroform, or other similar agent.

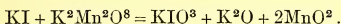
The weighed iodine compound is brought into a stoppered flask and chlorine water delivered from a large burette in excess, that is, until all yellow colour has disappeared; a drop of the mixture brought in contact with a drop of starch liquor produces no blue colour; sodic bicarbonate is then added till the mixture is neutral or slightly alkaline, together with potassic iodide and starch; the blue colour is then removed by $\frac{N}{100}$ hyposulphite; the strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 0.010108 gm. iodine, instead of 0.01 gm.

3. Estimation by Permanganate.

Reinige (Zeitschrift für An. Chem. ix. p. 39) has devised a process for estimating iodine in presence of bromides and chlorides which seems perfectly satisfactory.

When potassic iodide and permanganate are mixed, the rose colour of the latter disappears, a brown precipitate of manganic peroxide results, and free potash with potassic iodate remain in solution. 1 at. I = 127 reacts on 1 at. $K^2Mn^2O^8 = 316$, thus—



Heat accelerates the reaction, and it is advisable, especially with weak solutions, to add a small quantity of potassic carbonate to increase the alkalinity. No organic matter must be present.

Reinige has tested the process as follows :—A solution of iodine was prepared by dissolving the substance in caustic potash, so that 30 cc. of the mixture = 1.0 gm. I.

The standard permanganate was of such strength that 500 c.c. = 2.0 gm. permanganate crystals.

A standard solution of sodic hyposulphite was made of equal strength as the permanganate. Instead of preparing these solutions, it is manifest that the usual $\frac{N}{10}$ will be preferable.

Process : 30 c.c. iodine solution = 1.0 gm. I. was put into a flask with 506 c.c. permanganate, boiled for a few minutes, the precipitate

allowed to settle (which it does quickly), and the rose colour of the clear liquid removed by hyposulphite, of which 5.5 c.c. were necessary. 500.5 c.c. permanganate were therefore required = 1.001 gm. I.

The experiment was repeated with the addition of about 4 gm. caustic potash; the results were equally good. The same with potassic carbonate.

To prove the accuracy of the process in a mixture of iodides, bromides, and chlorides, with excess of alkali, the following experiment was made. 7 gm. commercial potassic bromide, the same of sodic chloride, with 1 gm. each of carbonate and caustic potash, were dissolved in a convenient quantity of water, and heated to boiling; permanganate was then added cautiously to destroy the traces of iodine and other impurities affecting the permanganate so long as decoloration took place; the slightest excess showed a green colour (manganate); to the mixture was then added 0.1246 gm. pure iodine, and the titration continued as at first described; the result was 0.125 gm. I. With systematic solutions of permanganate and hyposulphite, the calculation is as follows:—

$$1 \text{ c.c. } \frac{N}{10} \text{ solution} = 0.0127 \text{ gm. I.}$$

CHLORATES, IODATES, AND BROMATES.

Chloric acid, $\text{Cl}^2\text{O}^5 = 151$. Iodic acid, $\text{I}^2\text{O}^5 = 334$.

Bromic acid, $\text{Br}^2\text{O}^5 = 240$.

§ 67. THE compounds of chloric, iodic, and bromic acids may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective acids taken as monobasic, or their compounds, liberate 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while iodous and bromous chlorides remain in the retort. In both these cases digestion is preferable to distillation.

Among these substances chloric acid, in the form of potassic chlorate, is the only body of commercial importance, therefore the following example only is given as a specimen of the accuracy of the method of analysis:—0.2033 gm. pure potassic chlorate, equal to the sixth part of $\frac{1}{16\frac{1}{10}\frac{1}{6}}$ at., was decomposed by digestion with

potassic iodide and strong hydrochloric acid in the bottle shown in fig. 24; after the reaction was complete, and the bottle cold, the stopper was removed, and the contents washed out into a beaker; starch added, and 103 c.c. $\frac{N}{10}$ hyposulphite delivered in from the burette; then again 28.2 c.c. of $\frac{N}{100}$ iodine solution, to reproduce the blue colour; this latter was therefore equal to 2.32 c.c. $\frac{N}{10}$ iodine, which deducted from the 103 c.c. hyposulphite gave 100.68 c.c., which multiplied by the factor 0.002033, gave 0.2036 gm. instead of 0.2033 gm.

Potassic iodate and bromate gave equally sharp results.

CHLORINE.

Cl. = 35.5.

Chlorine Gas.

1 c.c. or 1 dm. $\frac{N}{10}$ arsenious or hyposulphite solution
= 0.00355 gm., or 0.0355 grn. Cl.

1 litre of chlorine at. 0° C., or 32° F., and .76 m.m., weighs
3.17 gm.

§ 68. CHLORINE water can be titrated with hyposulphite by adding a measured quantity of it to a solution of potassic iodide, then delivering the hyposulphite from a burette till the colour of the free iodine has disappeared; or by using an excess of the reducing agent, then starch liquor, and titrating residually with $\frac{N}{10}$ iodine. When arsenious solution is used for titration, the chlorine water is delivered into a solution of sodic carbonate, excess of arsenic added, then starch liquor and $\frac{N}{10}$ iodine till the colour appears, or the iodised starch paper may be used, § 33.

COMPOUNDS OF HYPOCHLOROUS ACID.

Chloride of Lime or Bleaching Powder, Chloride of Soda, &c.

§ 69. THE only substance of importance under this head is the so-called chloride of lime, used in very large quantities for bleaching purposes. The estimation of the free chlorine contained in it presents no difficulty when the arsenious solution is used for titration.

Commercial bleaching powder consists of a mixture in variable proportions of hypochlorite of lime (the true bleaching agent), calcic chloride, and hydrate of lime; it is generally valued and sold in this country by its percentage of chlorine. In France it is sold by degrees calculated from the volume of gaseous chlorine: 100° French = 31.78% English.

1. Estimation by Arsenious Solution.

The first thing to be done in determining the value of a sample of bleaching powder is to bring it into solution, which is best managed as follows :—

The sample is well and quickly mixed, and 10 gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream ; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a litre flask, the sediment again rubbed with water, poured off, and so on repeatedly until the whole of the chloride has been conveyed into the flask without loss, and the mortar washed quite clean ; the flask is then filled to the mark with water, well shaken, and 100 c.c. of the milky liquid taken out with a pipette, emptied into a beaker, and the $\frac{N}{10}$ arsenious solution delivered in from a burette until a drop of the mixture taken out with a glass rod, and brought in contact with the prepared starch paper, § 33. 1, gives no blue stain.

The starch paper may be dispensed with by adding arsenious solution in excess, then starch liquor, and titrating residually with $\frac{N}{10}$ iodine till the blue colour appears, the number of c.c. of arsenic used, multiplied by the factor 0.00355, will give the percentage of chlorine.

Example : 100 c.c. of chloride of lime liquid prepared as above directed were put into a beaker, and 86 c.c. of arsenious solution added, then starch liquor and 1.5 c.c. of $\frac{N}{10}$ iodine to produce the blue colour = 84.5 c.c. of arsenious solution, which multiplied by 0.00355 gave 0.2999 ; and as 1 gm. of the sample was contained in the 100 c.c., 29.99 per cent of chlorine.

Another 100 c.c. was carefully titrated with arsenious solution by the aid of iodised starch paper. 84.5 c.c. were required, also equal to 29.99%. Some recommend that the mixture of chloride of lime and water should be allowed to stand till clear, and the clear liquid only used for titration ; but this invariably gives lower results than when the milky mixture is used.

Instead of weighing 10 gm. of the sample, and using a c.c. burette, 100 grains may be weighed, diluted to 10,000 grains, and 1000 grains of the liquid = 100 dm. taken for titration ; the arsenious solution is then delivered from a decem burette ; the number of decems used multiplied by the factor 0.0355, will be the percentage of chlorine.

By weighing 3.55 gm. or 35.5 grn. of the sample, and diluting to

1 litre or 10,000 grains respectively ; then taking 100 c.c. or dm. for titration, the number of c.c. or dm. of arsenious solution required will be the percentage of chlorine direct.

2. Bunsen's Method (results accurate).

10 or 20 c.c. of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of potassic iodide added ; the mixture is then diluted somewhat, acidified with hydrochloric acid, and the liberated iodine titrated as in § 31. 4. 1 at. iodine so found represents 1 at. chlorine.

This is an exceedingly ready and accurate method of valuing the substance.

SULPHUR.

$$S = 32.$$

$$\begin{array}{lcl} 1 \text{ c.c. } \frac{N}{10} \text{ solution} & = & 0\cdot0016 \text{ gm. S} \\ \text{,,} & \text{,,} & 0\cdot0032 \text{ gm. SO}^2 \end{array}$$

§ 70. 1. WHEN sulphuretted hydrogen is brought in contact with solution of iodine, hydriodic acid is formed, and sulphur set free, ($HS^2 + 2I = 2IH + S$).

If the solutions are concentrated, a peculiar reddish colour occurs which hinders the correct ending of the reaction with starch ; the mixture must therefore be diluted freely with freshly boiled and cooled water ; the results are not very satisfactory. The determination of sulphuretted hydrogen is on this account preferably made with $\frac{N}{10}$ arsenious acid solution, described in § 33.

Sulphurous acid is very readily and very accurately estimated by $\frac{N}{10}$ iodine and starch, as also sulphites and hyposulphites. In the case of solution of sulphurous acid, however, the dilution must be such that not more than 0·04 per cent of SO^2 is present. The solutions of sulphites and hyposulphites need not be so much diluted. For the details of the reaction with hyposulphurous and sulphurous acids see § 31. In the determination of hyposulphites, the diatomic weight must be taken (expressed in centigrammes), in order that 1 c.c. of $\frac{N}{10}$ iodine solution shall be equal to 1 per cent of substance.

2. Estimation of Sulphur in Pyrites, Ores, Residues, &c.

a. By conversion into sulphuric acid, and titration with baric chloride.

The very finely powdered substance is introduced into a dry flask, together with about three or four times its weight of powdered

potassic chlorate, and small quantities of hydrochloric acid added from time to time, the mixture being finally warmed gently till all the sulphur has disappeared by being oxidised into sulphuric acid; the liquid is then diluted, filtered, and titrated as in § 38.

Or the substance may be fused with a mixture of potassic and sodic carbonates and potassic chlorate; the residue lixiviated with boiling water, filtered and titrated as above.

The use of potassic nitrate should be avoided, lest the precipitate of barytic sulphate should be contaminated with nitrate.

Storer recommends the treatment of copper or iron pyrites as follows:—

The finely powdered ore is covered with strong nitric acid, and potassic chlorate added in tolerably large proportion, heating the mixture on the water bath until all the sulphur is dissolved; then cooled and strong hydrochloric acid added, evaporated to dryness to separate the silica; then treated with boiling water to extract all soluble matter. This method is alleged to be quicker and more secure in decomposing the sulphur than by using hydrochloric acid and chlorate.

b. Alkalimetric Method (Pelouze).

This process, which is more especially designed for the rapid estimation of sulphur in iron and copper pyrites, is susceptible of very tolerable accuracy, the greatest variation from the truth not exceeding 1 or $1\frac{1}{2}\%$, when the manipulation is carefully performed.

The principle of the process is based on the fact, that when sulphur is ignited with potassic chlorate and sodic carbonate, the sulphur is converted by oxidation entirely into sulphuric acid, which expels its equivalent proportion of carbonic acid from the soda, forming neutral sodic sulphate; if, therefore, an accurately weighed quantity of the substance be fused with a known weight of pure sodic carbonate in excess, and the resulting mass titrated with normal acid, to find the quantity of unaltered carbonate, the proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate, and that actually required after the ignition.

For the sake of avoiding calculation, it is advisable to take 1 gm. of the finely levigated pyrites, and 5.3 gm. of pure sodic carbonate for each assay; and as 5.3 gm. sodic carbonate represents 100 c.c. of normal sulphuric acid ($=4.0$ gm. SO_3), it is only necessary to subtract the number of c.c. used after the ignition from

100, and multiply the remainder by the factor 0.016 (1 c.c. normal acid being equal to 0.016 gm. S), in order to arrive at the weight of sulphur in the 1 gm. of pyrites, and by moving the decimal point two places to the right, the percentage of that substance is obtained.

An example will show the details of the process and calculation.

Some cubes of iron pyrites were broken, and a small portion very finely powdered in a hardened steel mortar.

1 gm. of the powder was mixed *intimately* with 5.3 gm. pure sodic carbonate, and about 7 gm. each of potassic chlorate, and decrepitated chloride of sodium, in powder (the latter is added for the purpose of moderating the action), the whole was then introduced into a platinum crucible, and gradually exposed to a dull red heat for ten minutes; the crucible was then suffered to cool somewhat, and warm distilled water added; the solution so obtained was drawn off with a pipette and brought on a moistened filter, the process repeated five or six times, the residue then emptied into a beaker and boiled with a large quantity of water, the whole brought on the filter, and thoroughly washed with boiling water till all soluble matter was removed; the clear filtrate was then coloured with litmus, and titrated as in § 16. 67 c.c. of normal acid were required, which deducted from 100, left 33 c.c.; this multiplied by 0.016 gave 0.528 gm. sulphur, or 52.8%; pure FeS^2 contains 53.3%.

The insoluble ferric oxide remaining on the filter was dissolved in hydrochloric acid, reduced with zinc, and titrated with bichromate, as in § 30, yielding 46.5% iron; the determination of both substances occupied less than an hour, and the loss, supposing the pyrites to be pure, amounted to less than $\frac{3}{4}$ of a per cent.

If pure sodic carbonate is not at hand, the ordinary commercial article will answer the purpose, but the quantity of normal acid necessary to saturate it must of course be previously found. An iron spoon or ladle may also be used instead of the platinum crucible.

If roasted pyrites is to be examined by this method, it is unnecessary to add the salt, and equal quantities of the substance, sodic carbonate and potassic chlorate, may be taken for the combustion.

If the grain system of weights and measures are used, the quantity of pyrites will be 10 grains, and of carbonate 53 grains, each decem of normal acid being equal to 0.16 grn. sulphur.

It is not, of course, absolutely necessary that these quantities should be used, but less calculation is needed by this plan than any other.

Estimation of Sulphur in Pyrites by means of Cupric Oxide.

Kolb (*Jour. de Pharm. et de Chim.*, ser iv., vol. x. p. 401) has experimented very fully upon Pelouze's process, as described above, and found the sources of error to be various—formation of ferric sulphate, loss of chlorine, sulphur chloride, &c. The process recommended in its place, and which appears very satisfactory, consists in mixing with the finely powdered ore sodic carbonate and cupric oxide, and igniting the mixture in an iron, copper, or platinum vessel to a low red heat for about 15 minutes; the whole of the sulphur is oxidised to sulphuric acid, and combines quietly with the soda, the remaining unchanged sodic carbonate is then estimated by titration as usual. The method seems particularly applicable to roasted pyrites, the details of which are as follows:—

From 5 to 10 gm. of the ore, according to its richness in sulphur (if more than 10 per cent. 5 gm., less than 10 per cent. 10 gm.) is weighed and intimately mixed with 5 gm. sodic carbonate, and about 50 gm. dry cupric oxide, placed in the crucible and heated over a small gas-flame with frequent stirring for 12 or 15 minutes, the heat never exceeding a low red; the crucible is then cooled, the contents treated with hot water, filtered, and the filtrate and washings titrated with normal acid as usual.

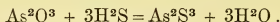
SULPHURETTED HYDROGEN.



$$\begin{array}{lcl} 1 \text{ c.c. } \frac{\text{N}}{10} \text{ arsenious acid} & = & 0.00255 \text{ gm. H}^2\text{S} \\ 1 \text{ dm.} & \text{,,} & \text{,,} = 0.0255 \text{ grn. ,,} \end{array}$$

Mohr's Method (results accurate).

§ 71. THIS residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine, as devised by Dupasquier. The principle is based on the fact, that when sulphuretted hydrogen is brought in contact with an excess of arsenious acid in solution, tersulphide of arsenic is formed; 1 eq. arsenious acid and 3 eq. sulphuretted hydrogen produce 1 eq. tersulphide of arsenic and 3 eq. water,



The excess of arsenious acid used is found by $\frac{\text{N}}{10}$ iodine and starch, as in § 33. In the case of estimating the strength of sulphuretted hydrogen water, the following plan may be pursued.

A measured quantity, say 10 c.c. $\frac{N}{10}$ arsenic solution, is put into a 300 c.c. flask, and 20 c.c. sulphuretted hydrogen water added, well mixed, and sufficient hydrochloric acid added to produce a distinct acid reaction; this produces a precipitate of tersulphide of arsenic, and the liquid itself is colourless. The whole is then diluted to 300 c.c., filtered through a dry filter into a dry vessel, 100 c.c. of the filtrate taken out and neutralised with sodic bicarbonate, then titrated with $\frac{N}{10}$ iodine and starch, as in § 33. 2; the quantity of arsenious acid so found is deducted from the original 10 c.c., and the remainder multiplied by the requisite factor for sulphuretted hydrogen.

The estimation of sulphuretted hydrogen contained in carburetted hydrogen gas, can by this method be made very accurately by leading the gas through the arsenic solution, or still better, through a dilute solution of caustic alkali, then adding arsenic solution, and titrating as before described. The apparatus devised by Mohr for this purpose is arranged as follows. The gas from a common burner is led by means of a vulcanised tube into two successive small wash bottles, containing the alkaline solution; from the last of these it is led into a large Woulf's bottle filled with water; the bottle has two necks, and a tap at the bottom, one of the necks contains the cork through which the tube carrying the gas is passed; the other, a cork through which a good-sized funnel with a tube reaching to the bottom of the bottle is passed; when the gas begins to bubble through the flasks, the tap is opened so as to allow the water to drop rapidly; if the pressure of gas is strong, the funnel tube acts as a safety valve, and allows the water to rise up into the cup of the funnel; when a sufficient quantity of gas has passed into the bottle, say six or eight pints, the water which has issued from the tap into some convenient vessel, is measured into cubic inches or litres, and gives the quantity of gas which has displaced it. In order to insure accurate measurement, all parts of the apparatus must be tight.

The flasks are then separated, and into the second, 5 c.c. of arsenic solution placed, and acidified slightly with hydrochloric acid; if any traces of a precipitate occur it is set aside for titration with the contents of the first flask, into which 10 c.c. or so of arsenic are put, acidified as before, both mixed together, diluted to a given measure, filtered, and a measured quantity titrated as before described.

PHOSPHORIC ACID.

$$P^2O^5 = 142.$$

1. By Precipitation as Uranic Phosphate with Potassic Ferrocyanide as Indicator.

§ 72. THIS method is based on the fact that when uranic nitrate or acetate is added to a solution of tribasic phosphoric acid containing ammoniac acetate and free acetic acid, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, having a light lemon colour, and the composition $2(Ur^{2}O^3), 2NH^4O, P^2O^5 + Aq.$ When this precipitate is washed with hot water, dried and burned, the ammonia is entirely dissipated, leaving uranic phosphate, which possesses the formula $2(Ur^{2}O^3), P^2O^5$, and contains in 100 parts 80.09 uranic oxide and 19.91 phosphoric acid. In the presence of fixed alkalis, instead of ammonia, the precipitate consists simply of uranic phosphate. By this method phosphoric acid may be completely removed from all the alkalis and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the process were fully described by me in the "Chemical News," February 4th, 1860, and immediately after the publication of that article, while employed in further investigation of the subject, I devised the volumetric method now to be described. Since that time it has come to my knowledge that Neubauer and Pincus had independently of each other and myself, arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that of measure, when the delicate reaction between uranium and potassic ferrocyanide is known. Moreover, the great want of a really good volumetric process for phosphoric acid in place of those hitherto used, has been felt by all who have anything to do with it, and consequently the most would be made of any new method possessing so great a claim to accuracy as the ordinary estimation of phosphoric acid by uranium undoubtedly does.

Neubauer appears to have been the earliest discoverer of the method. ("Archiv. für wissenschaftliche Heilkunde," Bd. iv. p. 228.) The experiments of Pincus were announced in the "Journal für Prakt. Chem.," 76, 104, neither of which publications have I been able to obtain. My own were not publicly described, inas-

much as the preparation of this book was in hand, and the process intended for insertion here.

The great advantages possessed by the method over Liebig's and Raewsky's iron process are that the combination between the phosphoric acid and uranium is definite and certain, and that the mixture needs no filtration, since uranic phosphate produces no colour with potassic ferrocyanide, like ferric phosphate. For the ready and accurate determination of phosphoric acid in manures and urine, the process is very serviceable.

Preparation of Standard Solutions.

Standard sodic phosphate. 50.422 gm. of pure crystallised sodic phosphate freed from extraneous moisture by powdering and pressing between sheets of filtering paper, are dissolved in water, and the solution diluted to 1 litre; or 504.2 grains to 1000 dm., 1 c.c., or 1 dm. of the solution so obtained = 0.01 gm., or 0.1 gm. P^2O^5 .

2. Standard Solution of Uranic Nitrate.

This solution, to correspond theoretically with the foregoing solution of sodic phosphate, should contain 44 gm. uranic oxide, equal to 71 gm. uranic nitrate per litre; but as the salt is difficult to obtain in a definite state of hydration, the strength of the solution must always be arranged by actual experiment. Dissolve therefore about 70 gm. nitrate in about 900 c.c. of distilled water. Uranic acetate would on some accounts be found preferable to the nitrate, but as this salt is liable to decomposition by light, or by impurities in the acetic acid, and is, moreover, much less soluble than the nitrate, the latter should be used; but it must be borne in mind that in using the nitrate, when the combination takes place between it and the phosphate, nitric acid is set free to combine with the alkaline base; and in order to prevent any irregularity from this circumstance, it is advisable to have sodic or ammoniac acetate present during the titration, so as to insure the combination of all the nitric acid with soda or ammonia; the acetic acid so set free has no solvent effect upon the uranic phosphate produced as would be the case with any mineral acid. There are also required,

3. Acid Solution of Sodic Acetate.

Dissolve 100 gm. sodic acetate in water; add 100 c.c. strong acetic acid, and dilute to 1 litre.

4. Some finely powdered Yellow Potassic Prussiate, or a freshly prepared solution of the same. 1—20.

5. Titration of the Uranic Solution.

Measure 20 c.c. of the standard sodic phosphate into a small beaker, and add 5 c.c. of sodic acetate solution, and about 25 c.c. of water, making altogether 50 c.c., or thereabouts; heat on the water bath to about 80° C., then run into it 15 or 16 c.c. of the uranic solution from a $\frac{1}{5}$ or $\frac{1}{10}$ c.c. Mohr's burette; stir well with a thin glass rod, and bring a drop of the mixture on the point of the rod upon a white porcelain slab or plate, then with a thin glass rod, or better, a piece of platinum wire moistened with the breath, bring the smallest particle of the powdered yellow prussiate, or a droplet of the solution, into the middle of the drop, and wait a moment to see if any brown colour, however faint, appears. Should this not occur, add cautiously more uranic solution until the coloration does occur in fresh drops, tested from time to time. Repeat the experiment with a fresh portion to be certain of the exact point, then read off the burette. Suppose 18.7 c.c. of the uranic solution have been required to produce the colour, with 20 c.c. phosphate solution, then every 18.7 c.c. will have to be diluted to 20 c.c. in order to be of the proper strength—or 187 to 200, or 935 to 1000. After dilution, a fresh trial ought to be made to insure accuracy.

It is of considerable importance that the actual experiment for estimating phosphoric acid by means of the uranic solution should take place with about the same bulk of fluid that has been used in standardising the solution, and with as near as possible the same relative amount of sodic acetate, and the production of the same depth of colour in testing. If these conditions are observed, the method is really capable of extreme accuracy.

A little practice enables the operator to tell very quickly the precise point, but it must be remembered that when the two drops are brought together for the production of the chocolate colour, however faint it seems at first, if left for some little time, the colour increases considerably, owing to the retarding action of the sodic acetate and acetic acid upon the formation of uranic ferrocyanide, but this has no effect upon the accuracy of the process, since the original standard of the solution has been based on an experiment conducted in precisely the same way.

6. Example of Analysis.

20 c.c. sodic phosphate solution were carefully precipitated by magnesia solution, and yielded magnesian pyrophosphate = 0.199 gm. P^2O^5 .

20 c.c. were then titrated with standard uranic solution, 20.1 c.c. being required to produce the faint brown colour ; the mixture was then boiled, washed by decantation through a filter, then collected, dried, and ignited, yielding 1.007 gm. $2Ur^2O^3$, $P^2O^5 = 0.2014$ gm. P^2O^5 . 1 c.c. of uranic solution may, therefore, fairly be taken as equal to 0.01 gm. P^2O^5 .

The process is applicable, volumetrically, to all phosphates of the first and second groups, but not to any of the so-called sesquioxides, having the formula M^2O^3 , nor is it available in the presence of arsenic acid or any metals giving coloured precipitates with potassic ferrocyanide, such as copper, &c.

The so-called superphosphates of lime and other manures containing monocalcic phosphate are very readily examined by this method—since it is only necessary to exhaust them at first with cold, and lastly with warm water ; add ammonia to neutralise the free acid in the liquid, then sodic acetate and acetic acid in excess, and titrate at once. Iron or alumina, if present in the manure, will not be found, generally speaking, in the watery extract, or if so, only in very slight traces, and will be left insoluble on the addition of the acetic acid. Should this be the case to any extent, it is best to filter off the precipitate and estimate it by weight as phosphate of iron, taking a measured portion of the filtrate for titration with uranium. When the watery solution is highly coloured with organic matter, it should be evaporated to dryness with a little nitric acid, then redissolved for titration.

Bones and bone-ash are dissolved in hydrochloric acid ; the phosphates of lime and magnesia precipitated with ammonia, redissolved in acetic acid, sodic acetate added, then titrated as before.

Manures or other phosphoric acid compounds containing iron or alumina or both, are best dissolved in hydrochloric acid, and the whole of the phosphoric acid precipitated as a mixture of phosphates of lime, magnesia, iron, and alumina, by ammonia in excess ; the precipitate is brought upon a filter and the liquid drained away, the precipitate slightly washed, and when sufficiently drained it is treated two or three times with acetic acid on the filter, then washed, and the filtrate and washings containing all the phosphate

of lime and magnesia collected and set aside. The residue on the filter, consisting of phosphate of iron and alumina, is dissolved on the filter with hydrochloric acid, the filter washed clean, and the acid filtrate and washings mixed with a tolerable quantity of tartaric acid, then a clear solution of ammonia, ammoniac chloride, and magnesian sulphate, added in excess to separate all the phosphoric acid as double phosphate of magnesia and ammonia; the solution should be allowed to stand four or five hours in a slightly warm place, the precipitate then collected in a filter, washed with ammoniacal water, then dissolved on a filter with acetic acid, and the solution so obtained mixed with the former liquid, and titrated with uranium as before described; the result gives the total amount of phosphoric acid present.

If lime only is present with the iron and alumina it is preferable to precipitate it first as oxalate, by adding ammoniac oxalate and acetate (the latter in good quantity) to the hydrochloric acid solution. The filtrate and washings are then treated with the tartarised magnesia solution to precipitate all the phosphoric acid.

Magnesian Solution for precipitating Phosphoric Acid.

Crystallised magnesian sulphate	1 part
Pure ammoniac chloride	1 „
Distilled water	8 „
Solution of ammonia 10% (.96 sp. gr.)	4 „

After standing a few days filter for use.

Tartarised Magnesian Solution for precipitating Phosphoric Acid in the presence of Iron and Alumina.

Crystallised magnesian sulphate	12 parts
„ tartaric acid	15 „
Pure ammoniac chloride	16 „
Water	1000 „

Where the amounts of iron and alumina are very large in comparison with the phosphoric acid, it is better to adopt the method of separation originally proposed by Reynoso and afterwards modified by Girard, namely, by tin.

To the solution of the substance in nitric acid pure granulated metallic tin is added, in the proportion of five or six parts to every part of phosphoric acid supposed to be present, and the mixture digested on the water bath for two or three hours; the fluid is then carefully decanted off through a filter, and repeatedly

washed by decantation with hot water; yellow ammoniac sulphide is then added to the precipitate in the beaker to dissolve all the phosphate of tin, and whatever traces may have been retained on the filter are removed by eventually passing the sulphide solution through it; the insoluble compounds of alumina and iron are thus retained on the original filter, and washed with water containing ammoniac sulphide. Magnesia solution is then added to the clear greenish-yellow filtrate and washings, to precipitate all the phosphoric acid as double phosphate of magnesia and ammonia, which is collected, washed with ammoniacal water, dissolved in acetic acid, and titrated with uranium as before described.

Instead of the tin method as just described, a modification of Chancel's bismuth process has given exceedingly good results in separating phosphoric acid from iron and alumina. It has been especially used in the estimation of P^2O^5 in the German phosphates, phosphorite, native phosphate of alumina, &c.; and in comparison with the molybdic and magnesia processes by weight, has given equally accurate results in a very much shorter time. (See Birnbaum Zeitschrift für an Chem., vol. ix. p. 203.)

The method is as follows:—2 gm. of the very finely powdered mineral is covered with 6–7 c.c. pure nitric acid, sp. gr. 1.25, and kept at about 90° C. for twenty minutes, then diluted with water and filtered. The filtrate is diluted to 500 c.c.—sufficient for five separate estimations if required—100 c.c. only being taken, equal to 0.4 gm. mineral. The 100 c.c. are diluted with the same volume of water, the fluid then brought to boiling, and precipitated with a solution of bismuthic nitrate prepared in the following manner:—Crystals of bismuthic nitrate are treated with water and just so much nitric acid added that on further dilution with water no milkiness takes place, the proportion of bismuth should be about 25 gm. per litre; sufficient of this solution being added to combine with all the P^2O^5 , the vessel is set aside to cool, by which means the precipitate becomes crystalline, and moreover, the whole of the bismuthic phosphate will be separated from the fluid, which would not be the case in the hot liquid. The fluid is decanted through a filter, adding cold water repeatedly to the main precipitate in the beaker, and pouring off; when sufficiently washed, the filtrate is treated with a few drops of hydrochloric acid to dissolve the small quantity of precipitate upon it, washed, and the fluid so obtained mixed with the main precipitate. Ammonia, and ammoniac sulphide are then added in tolerable quantity, and the

mixture digested till the precipitate is quite black ; acetic acid in excess is then added, and the mixture heated nearly to boiling for a short time, filtered when settled clear, washed, the remaining traces of H^2S in the fluid removed by a little chlorine water, and then titrated with uranic solution as usual.

The titration with uranium must be adopted, since the bismuthic precipitate is not of constant composition ; however, it contains all the P^2O^5 in the original compound, and can be recovered as ammoniac phosphate, the bismuth being all removed as sulphide. It is absolutely necessary that no hydrochloric or sulphuric acid is present in the original solution in which the precipitation takes place.

Special methods of estimating soluble or monocalcic phosphate and tricalcic phosphate will be found in the section on manures.

As uranium is somewhat costly, it is well to collect the precipitates, where many analyses are made, in a large bottle, and when sufficient has been obtained, to recover the uranium for the same purpose, as follows :—Collect the uranic phosphate, and wash well with boiling water on a filter, then dry and weigh roughly. It is then dissolved in tolerably strong nitric acid, and half its weight of granulated metallic tin added, then heated until all the tin is converted into oxide ; the precipitate will contain all the P^2O^5 in combination with the tin. A few drops of the clear liquid should give no permanent precipitate with ammonia ; if it does, more tin must be added, and again heated. The liquid is then filtered off—evaporated to expel any nitric acid—sulphuretted hydrogen passed through for a short time, filtered, evaporated, and set aside, that the uranic nitrate may crystallise out.

TANNIC ACID.

§ 73. THE estimation of tannin in the various astringent materials used in tanning by volumetric methods is not of the most satisfactory character. A great variety have been proposed, the best of which appear to be the gelatine process, as modified by Mulder, and Gerland's process, by means of a standard solution of tartar emetic.

Watts (Pharm. Journ., March 1867), who has had considerable experience in the valuation of tanning materials, thus describes the two processes alluded to :—

1. Analysis by Standard Gelatine (applicable only to Woods, Bark, Roots, and Leaves).

Preparation of Standard Solutions.

Dissolve in a litre of water 3 gm. of isinglass, and add to it about 1 gm. of powdered alum. To ascertain the quantity of tannin which 1 c.c. of this solution represents, dissolve 2 gm. of tannic acid accurately in 1 litre of water for a standard solution, of which every 10 c.c. will therefore contain 0.02 gm. of tannic acid. Measure now 50 c.c. of this latter solution, containing 0.1 gm. of acid, into a beaker; dilute it somewhat with water, and drop in from a burette the aluminous solution until the falling of a drop on the surface no longer produces the characteristic ring of tannate of gelatine, then allow the precipitate to settle; next take a drop out carefully by the end of a glass rod, drop it on to the surface of a black glass plate, and there test it for excess of either tannin or gelatine, by bringing in contact with it a drop of either solution, and observing whether any cloudiness occur at the junction of the two drops; when the exact point has been ascertained at which the gelatine no longer produces a precipitate, which requires some practice to hit exactly, the number of cubic centimetres of gelatine solution consumed correspond to 0.1 gm. of tannic acid.

In examining various materials by this process, they should be brought into a powdered state, and exhausted with hot water, pouring off the clear portions, but not filtering.

2. Gerland's Antimonial Process (applicable to the same materials as above, and also Kino, Catechu, &c.)

The solution of antimonial tartrate may be made by weighing 2.611 gm. of emetic tartar dried at 100° C. in a litre of water. 1 c.c. = 0.005 gm. pure tannin.

It is safer, however, to titrate a solution of the salt upon the same standard tannin solution, as described above, for the gelatine process.

50 c.c. of the tannin solution, = 0.1 gm. tannin, is placed in a beaker, and a few drops of saturated solution of ammoniac chloride added; then the antimonial solution run in precisely as described for the gelatine process, using a plate of black glass to ascertain which is in excess.

The ammonium salt is found to aid the separation of the precipitate of tannate of antimony very considerably, in the same way, probably, as the alum assists the gelatine process.

Watts modifies the procedure as follows :—

“To ascertain the approximate amount of antimony solution required by a certain quantity of material, I take six beakers, and having exhausted, say 60 gm. of astringent substance, make the decoction up to 600 c.c. I then measure 100 c.c. of it into each beaker, in order that the soluble portions of 10 gm. of substance may be contained in each. 10 c.c. of antimony solution are then run into the first, 15 into the second, 20 into the third, and so on ; by testing then each beaker as before explained, it is very easy to see in which there is an excess of tannin, and in which an excess of antimony. Thus, if the beaker which contains 15 c.c. of antimony, should, on testing, indicate the presence of tannic acid, while that which has 20 c.c. shows an excess of the former, it is obvious that 10 gm. of the substance used will require for the precipitation of its tannin a quantity of tartar-emetic solution lying between 15 and 20 c.c. ; by exhausting some fresh material, and operating over again, the exact point of precipitation will be very readily obtained.

“The analysis of catechus and kinos, by this method, still presents some difficulty, and to coax the precipitate into subsiding will tax the patience of most operators ; sometimes the addition of a little alum or a few c.c. of alcohol will effect it, and I have found that merely warming the solution gently for a few minutes will sometimes cause the precipitate to settle sufficiently, so as to enable it to be tested as above ; but in all cases it will be found rather more tedious than when working upon such bodies as oak bark, or its analogues.

“This process possesses the same advantage as the gelatine, in not precipitating gallic acid, and excels it in the fact that the precipitate is denser, and more readily subsides.”

SUGAR.

§ 74. THE term sugar is applied to several bodies possessing distinct properties, and differing somewhat in chemical composition. There are only two classes, however, of general importance, that is to say :—

1. Those that possess the chemical composition of grape sugar or glucose, $C^6H^{12}O^6$, such as the sugar contained in the juice of grapes, apples, and other ripe fruit ; also that which occurs in urine in *Diabetes mellitus*.

2. Common cane sugar, $C^{12}H^{22}O^{11}$, contained in the juice of the sugar cane, beet root, maple, &c.

Sugars of the latter class, and also those contained in milk, dextrine, &c., may all be converted into grape sugar by boiling with weak sulphuric acid, and must all be so converted before they can be estimated by the chemical method here given.

This method is based on the fact, that although a mixture of pure cupric sulphate, potassic tartrate, and caustic soda, mixed in proper proportions, may be boiled without undergoing change; yet, if only a trace of grape sugar be added, a very slight warming is enough to precipitate a portion of the copper as protoxide, Cu^2O .

Fehling, Neubauer, and others, have very carefully examined the reaction which takes place, and found that 1 at. pure grape sugar = 180, is capable of reducing exactly 5 at. = 397 of cupric oxide (CuO) to the state of cuprous oxide (Cu^2O). Therefore, if the quantity of copper reduced by a given solution of sugar is known, it is easy to find the quantity of sugar present.

There are two methods of procedure—

1. To prepare a standard solution of pure cupric sulphate with potassic tartrate and caustic soda, and add the sugar solution to a definite quantity of it until the deep blue colour has disappeared; or—

2. To add the copper solution, which may be of indefinite strength, in excess, and estimate the precipitated protoxide, either by weight or indirectly, by the method of Schwarz, § 47.

As the first method is susceptible of very accurate results, and occupies little time, it is generally preferred. The requirements are as follows:—

Standard Solution of Copper. 34.64 gm. of pure crystallised cupric sulphate, previously powdered and pressed between blotting paper, are weighed and dissolved in 200 c.c. of distilled water; in another vessel, 173 gm. of pure crystals of Rochelle salt are dissolved in 480 c.c. of solution of pure caustic soda, sp. gr. 1.14. The two solutions are then mixed, and the deep clear blue solution diluted with distilled water to 1 litre.

Löwe advocates the use of glycerine instead of alkaline tartrate in making this solution (*Zeitschrift für an Chem.*, ix. p. 20), using about 20 gm. glycerine for the amount of copper above described. The solution so made, however, will not bear much diluting without becoming turbid, and as glycerine is frequently contaminated with sugar as an adulteration, the modification does not seem to possess any advantage over the original method.

Each 10 c.c. of the solution so prepared, containing 0.3464 gm.

cupric sulphate, represent exactly 0.050 gm. pure anhydrous grape sugar. It must be preserved in a dark place, and in well-stoppered bottles, kept tolerably full, since, if the solution absorbs much carbonic acid, a precipitate will occur in boiling even in the absence of sugar. This may, however, be prevented by adding fresh caustic alkali. In all cases, before using it for titrating a solution of sugar, 10 c.c. should be boiled with about 40 c.c. of water, for a few minutes, in order to be certain of its fitness.

1. The Solution of Sugar.

This must be so diluted as to contain $\frac{1}{2}$ or at most 1% sugar; if on trial it is found to be stronger than this, it must be further diluted with a measured quantity of distilled water.

If the sugar solution to be examined is of dark colour, or likely to contain extractive matters which might interfere with the distinct ending of the reaction, it is advisable to heat a measured quantity to boiling, and add a few drops of milk of lime, allow the precipitate to settle, then filter through animal charcoal, and dilute with the washings to a definite volume.

From thick mucilaginous liquids, or those which contain a large proportion of albuminous or extractive matters, the sugar is best extracted by Graham's dialyser.

The method may be applied directly to diabetic urine (see § 78. 7), as also to brewer's wort or distiller's mash. Dextrine does not interfere, except the boiling of the liquid under titration is long continued.

Cane, beet, and maple sugar juice, or prepared sugars, are converted into grape sugar by heating 30 or 40 c.c. of the clarified liquid in a water bath, with 30 or 40 drops of dilute sulphuric acid, (1 to 5), for an hour or two, replacing the evaporated water from time to time, so as not to char the sugar; the acid is then neutralised with sodic carbonate, and the liquid diluted to 15 or 20 times its volume before being titrated.

100 parts grape sugar so found represent 95 parts cane or beet sugar, or 10 c.c. copper solution are reduced by 0.0475 gm. cane or beet sugar. Starch or dextrine, or substances containing them, require to be heated longer with the acid in order to insure their conversion into glucose. To convert 1 gm. starch into dextrine, and thence into sugar, it should be mixed with 10 c.c. cold water, smoothly, then heated gently until thick, then add 12 drops dilute acid as before, and boil in a small flask, supported obliquely on a

sand-bath for 8 or 10 hours, replacing the water from time to time ; then neutralise and dilute as before.

The change may be produced more rapidly and at lower temperature by using some form of diastase in place of sulphuric acid ; an infusion of malt is best suited to the purpose, but the temperature must not exceed 71° C. (160° Fahr.) ; about four hours' digestion is sufficient. A like quantity of the same malt solution must be digested alone, at the same temperature, and titrated for its amount of sugar, which is deducted from the total quantity found in the mixture.

100 parts of grape sugar so found represent 90 parts of starch or dextrine ($C^6H^{10}O^5$)_n, or 10 c.c. copper solution, are reduced by 0.45 gm. starch or dextrine. When dextrine is present with grape sugar, care must be taken not to boil the mixture too long with the alkaline copper solution, as it has been found that a small portion of the copper is precipitated by the dextrine (Rumpf and Heinzerling *Zeitschrift für an Chem.*, ix. 358.)

Sugar of milk ($C^{12}H^{22}O^{11}$) may also be converted into grape sugar by boiling for a short time with dilute sulphuric acid, before being estimated.

2. The Analytical Process.

10 c.c. of the copper solution are measured into a convenient-sized flask or a white porcelain dish, and diluted with 40 c.c. of water, or, if necessary, the same quantity of dilute caustic soda, and brought to gentle boiling. The dilute sugar solution is then delivered in from time to time from a graduated burette ; when the precipitated oxide appears of a bright red colour, the lamp should be removed and the precipitate allowed to settle ; if the flask is then held before a window, or the dish lifted on one side so as to cause the clear liquid to flow against the white porcelain, the colour may readily be seen ; should any blue tinge remain, more sugar solution is added, and the boiling recommenced and continued until all colour just disappears. If any doubt exists, a small portion of the *hot* mixture should be filtered, acidified with acetic acid, and a drop of solution of potassic ferrocyanide added ; if copper is in excess, a brown colour or precipitate will be produced.

It is almost impossible to hit the exact point on the first trial, but it affords a very good guide for a more exact titration the second time ; the quantity of sugar solution necessary to discharge the colour from 10 c.c. copper solution contains 0.05 gm. grape sugar.

SILVER.

Ag. = 108.

1 c.c. or 1 dm. $\frac{N}{10}$ solution of sodic chloride = 0.0108 gm. or 0.108 grn. metallic silver ; also 0.0171 gm. or 0.171 grn. silver nitrate.

Decinormal Solution of Sodic Chloride.—See Sect. 35. 2.

Decinormal Solution of Silver.—See Sect. 35. 1.

§ 75. THE determination of silver is precisely the converse of the operations described under chlorine, and the process may either be concluded by adding the sodic chloride till no further precipitate is produced, or the potassic chromate may be used as indicator. In the latter case, however, it is advisable to add the salt solution in excess, then a drop or two of chromate solution, and titrate residually with $\frac{N}{10}$ silver solution, till the red colour is produced, for the excess of sodic chloride.

1. Analysis of the Silver Solutions used in Photography.

The silver bath solutions for sensitising collodion and paper frequently require examination, as their strength is constantly lessening. To save calculation, it is better to use an empirical solution of salt than the systematic one described above.

This is best prepared by dissolving 43 grains of pure sodic chloride in 10,000 grains of distilled water ; each decem (= 10 grs.) of this solution will precipitate 0.125 grn. (*i.e.* $\frac{1}{8}$ grn.) of pure silver nitrate ; therefore, if 1 fluid drachm of any silver solution be taken for examination, the number of decems of salt solution required to precipitate all the silver will be the number of grains of silver nitrate in each ounce of the solution.

Example : One fluid drachm of an old nitrate bath was carefully measured into a stoppered bottle, 10 or 15 drops of pure nitric acid and a little distilled water added ; the salt solution was then cautiously added, shaking well after each addition until no further precipitate was produced ; the quantity required was 26.5 dm. = $26\frac{1}{2}$ grains of silver nitrate in each ounce of solution.

Crystals of silver nitrate may also be examined in the same way, by dissolving say 30 or 40 grs. in an ounce of water, taking one drachm of the fluid and titrating as above.

In consequence of the rapidity and accuracy with which silver may be determined, when potassic chromate is used as indicator,

some may prefer to use that method. It is then necessary to have a standard solution of silver, of the same chemical power as the salt solution ; this is made by dissolving 125 grains of pure and dry neutral silver nitrate in 10,000 grs. of distilled water ; both solutions will then be equal, volume for volume.

Suppose, therefore, it is necessary to examine a silver solution used for sensitising paper. One drachm is measured, and if any free acid is present, cautiously neutralised with a weak solution of sodic carbonate ; 100 dm. of salt solution is then added with a pipette, if the solution is under 100 grs. to the ounce the quantity will be sufficient. 3 or 4 drops of chromate solution are then put in, and the silver solution delivered from the burette until the blood-red colour of chromate of silver is just visible. Suppose that 25·5 dm. have been required, let that number be deducted from the 100 dm. of salt solution, which will leave 74·5 dm., or $74\frac{1}{2}$ grains to the ounce.

This method is much more likely to give exact results in the hands of persons not expert in analysis than the ordinary plan by precipitation, inasmuch as with collodion baths, containing as they always do iodide of silver, it is almost impossible to get the supernatant liquid clear enough to distinguish the exact end of the analysis.

2. Estimation of Silver, in Ores and Alloys, by Starch Iodide.

Methods of Pisani and F. Field (very accurate in the absence of Mercury, Protoxides, and Salts of Tin, Iron, and Manganese, Antimony, Arsenious Acid, and Chloride of Gold).

If a solution of the blue starch iodide be added to a neutral solution of silver nitrate, while any of the latter is in excess the blue colour disappears, the iodine entering into combination with the silver ; as soon as all the silver is thus saturated, the blue colour remains permanent, and marks the end of the process ; the reaction is very delicate, and the process accurate in the absence of the metals and salts mentioned above, it is more especially applicable to the analysis of ores and alloys of silver containing lead and copper.

The solution of starch iodide, devised by Pisani, is made by rubbing together in a mortar 2 gm. iodine with 15 gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask, and digesting in a water-bath for about an hour, or until it has assumed a dark bluish-gray colour ; water is then added

till all is dissolved. The strength of the solution is then ascertained by titrating it with 10 c.c. of a solution of silver containing 1 gm. in the litre, to which a portion of pure precipitated calcic carbonate is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch solution should be of such a strength that about 50 c.c. is required for 10 c.c. of the silver solution ($= 0.01$ gm. silver).

F. Field ("Chem. News," vol. ii. p. 17), who discovered the principle of this method simultaneously with Pisani, uses a solution of iodine in potassic iodide with starch liquor. Those who desire to make use of this plan can use the deci and centinormal solutions of iodine described in the former part of this treatise, the results being the same in either case.

In the analysis of silver containing copper the solution must be considerably diluted in order to weaken the colour of the copper, a small measured portion is then taken, calcic carbonate added, and starch iodide till the colour is permanent. It is best to operate with about from 60 to 100 c.c., containing not more than 0.02 gm. silver; when the quantity is much greater than this, it is preferable to precipitate the greater portion with $\frac{N}{10}$ sodic chloride, and to complete with starch iodide after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid, and filter off the lead sulphate, then add calcic carbonate to neutralise excess of acid, filter again if necessary, then add fresh carbonate and titrate as above.

3. Assay of Commercial Silver (Plate, Bullion, Coin, &c.), Gay Lussac's Method modified by J. G. Mulder.

For more than thirty years Gay Lussac's method of estimating silver in its alloys has been practised intact, at all the European mints, under the name of the "humid method," in place of the old system of cupellation; during that time it has been regarded as one of the most exact methods of quantitative analysis; the researches of Mulder, however, into the innermost details of the process have shown that it is capable of even greater accuracy than has hitherto been gained by it. For the particulars of Mulder's investigations I cannot do better than refer the reader to the excellent translations of his memoir, translated in the "Chemical News," by Adriani.

The principle of the process is the same as described under the head of chlorine, depending on the affinity which that body has for

silver in preference to all other substances, and resulting in the formation of chloride of silver, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrious inventor of this process for assaying silver and which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established, it is the best plan of procedure; if, therefore, a standard solution of salt be made of such strength that 100 c.c. will exactly precipitate 1 gramme of silver, it is manifest that each $\frac{1}{10}$ c.c. will precipitate 1 milligramme or $\frac{1}{1000}$ th part of the gramme taken, and consequently in the analysis of 1 gramme of any alloy containing silver, the number of $\frac{1}{10}$ c.c. required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner, consequently a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 c.c. will exactly precipitate 1 gramme of silver, and, therefore, 1 c.c. one milligramme.

The silver alloy to be examined (the composition of which must be approximately known), is weighed so that about 1 gramme of pure silver is present, it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 c.c. of standard solution of salt added from a pipette in order to precipitate exactly 1 gm. of silver, the bottle containing the mixture is then well shaken until the chloride of silver has curdled, leaving the liquid clear.

The question is now—Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate is produced, 1 c.c. is delivered in, and after clearing, another, and so on as long as a precipitate is produced; if on the other hand the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 gm., a decimal solution of silver is used, prepared by dissolving 1 gm. pure silver in pure nitric acid and diluting to 1 litre, this solution is added after the same manner as the salt solution just described, until no further precipitate occurs; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 gm. of the alloy.

The process thus shortly described is that originally devised by Gay Lussac, and it was taken for granted that when equivalent chemical proportions of silver and sodic chloride were brought thus in contact that every trace of the metal was precipitated from the solution, leaving sodic nitrate and free nitric acid only in solution. The researches of Mulder, however, go to prove that this is not strictly the case, but that when the most exact chemical proportions of silver and salt are made to react on each other, and the chloride has subsided, a few drops more of either salt or silver solution will produce a further precipitate, indicating the presence of both silver nitrate and sodic chloride in a state of equilibrium, which is upset on the addition of either salt or silver. Mulder decides, and no doubt rightly, that this peculiarity is owing to the presence of sodic nitrate, and varies somewhat with the temperature and state of dilution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, until no further precipitate appears, the clear liquid will at this point give a precipitate with dilute silver solution, and if it be added till no further cloudiness is produced, it will again be precipitable by dilute salt solution.

For example : Suppose that in a given silver analysis the decimal salt solution has been added so long as a precipitate is produced, and that 1 c.c. (= 20 drops of Mulder's dropping apparatus) of decimal silver is in turn required to precipitate the apparent excess, it would be found that when this had been done, 1 c.c. more of salt solution would be wanted to reach the point at which no further cloudiness is produced by it, and so the changes might be rung time after time ; if, however, instead of the last 1 c.c. (= 20 drops) of salt, half the quantity be added, that is to say 10 drops (= $\frac{1}{2}$ c.c.); Mulder's so-called neutral point is reached, namely, that in which, if the liquid be divided in half, both salt and silver will produce the same amount of precipitate. At this stage the solution contains silver chloride dissolved in sodic nitrate, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

1. By adding decimal salt solution until it just ceases to produce a cloudiness.
2. By adding a slight excess of salt, and then decimal silver till no more precipitate occurs.
3. By finding the neutral point.

According to Mulder the latter is the only correct method, and preserves its accuracy at all temperatures up to 56° C. ($=133^{\circ}$ Fahr.) while the difference between 1 and 3 amounts to $\frac{1}{2}$ a milligramme, and that between 1 and 2 to 1 milligramme on 1 gramme of silver at 16° C. ($=60^{\circ}$ Fahr.) and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by Mulder's method than by that of Gay Lussac, but as a compensation, much greater accuracy is obtained.

On the whole, it appears to me preferable to weigh the alloy so that slightly more than 1 gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of a precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation—say 100.1 c.c. are found equal to 1 gm. silver, the operator has only to calculate that quantity of the salt solution in question for every 1 gm. silver he assays in the form of alloy, and the error produced by the solubility of silver chloride in sodic nitrate is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 17° C. $=62^{\circ}$ Fahr., this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment, for it requires a great expenditure of time and patience to reverse an assay two or three times, and each time cautiously adding the solutions, drop by drop, then shaking and waiting for the liquid to clear, beside the risk of discolouring the chloride of silver, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 gm. pure silver, then it is best to add once for all 2, 3, or 5 c.c., according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

The Standard Solutions and Necessary Apparatus.

a. Standard Solution of Salt. Pure sodic chloride is prepared by treating a concentrated solution of the whitest table salt first with a solution of caustic baryta to remove sulphuric acid and magnesia, then with a slight excess of sodic carbonate to remove baryta and lime, warming and allowing the precipitates to subside; then evaporating to a small bulk, that crystals may form; these are

separated by a filter, and slightly washed with cold distilled water ; dried, removed from the filter, and heated to dull redness, and when cold preserved in a well-closed bottle for use. The mother liquor is thrown away or used for other purposes. Of the salt so prepared, or of chemically pure rock-salt (Steinsalz, a substance to be obtained freely in Germany), 5·4145 gm. is to be weighed and dissolved in 1 litre of distilled water at $16^{\circ}\text{C.} = 60^{\circ}\text{Fahr.}$ 100 c.c. of this solution will precipitate exactly 1 gm. silver ; it is preserved in a well-stoppered bottle, and shaken before use.

Decimal Solution of Salt. 100 c.c. of the above solution is diluted to exactly 1 litre with distilled water at $16^{\circ}\text{C.} = 60^{\circ}\text{Fahr.}$ 1 c.c. will precipitate 0·001 gm. silver.

b. Decimal Solution of Silver. Pure metallic silver is best prepared by galvanic action from pure chloride ; and as clean and secure a method as any, is to wrap a lump of clean zinc, into which a silver wire is melted, with a piece of wetted bladder or calico, so as to keep any particles of impurity contained in the zinc from the silver. The chloride is placed at the bottom of a porcelain dish, covered with dilute sulphuric acid, and the zinc laid in the middle ; the silver wire is bent over so as to be immersed in the chloride ; as soon as the acid begins to act upon the zinc, the reduction commences in the chloride, and grows gradually all over the mass ; the resulting finely-divided silver is well washed, first with dilute acid, then with hot water, till all acid and soluble zinc are removed.

The moist metal is then mixed with a little sodic carbonate, salt-petre, and borax, say about an eighth part of each, and dried perfectly.

The metallic silver obtained as above is never free altogether from organic matter and undecomposed chloride, and, therefore, it must invariably be melted. Mulder recommends that the melting should be done in a porcelain crucible, immersed in sand contained in a common earthen crucible ; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the silver when melted no particles of dirt or sand may fall into it. If the quantity of metal is small it may be melted in a porcelain crucible over a gas blowpipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe-clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a gold-

smith's mill, in order that it may be readily cut for weighing ; the granulated metal is, of course, ready for use at once without any rolling.

1 gm. of this silver is dissolved in pure dilute nitric acid and diluted to 1 litre ; each c.c. contains 0.001 gm. silver ; it should be kept from the light.

Dropping Apparatus for concluding the Assay. Mulder constructs a special affair for this purpose, consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid, the delivery tube has an opening of such size that 20 drops measure exactly 1 c.c.—the vessel itself is not graduated. As this arrangement is of more service to assay than to general laboratories, it need not be further described here. A small burette divided in $\frac{1}{10}$ c.c. with a convenient dropping tube, will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100 c.c. pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 gm. of distilled water at 16° C.

The test bottles, holding about 200 c.c., should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be covered over the stopper.

c. Titration of the Standard Salt Solution. From what has been said previously as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt, containing 5.4145 gm. per litre, although this is chemically correct in its strength. The real working power must be found by experiment. From 1.002 to 1.004 gm. of absolutely pure silver is weighed on the assay balance, put into a test bottle with about 5 c.c. of pure nitric acid, about 1.2 sp. gr., and gently heated in the water or sand bath till it is all dissolved. The nitrous vapours are then blown from the bottle, and it is set aside to cool down to about 16° C. or 60° Fahr.

The 100 c.c. pipette, which should be securely fixed in a support, is then carefully filled with the salt solution, and delivered into the test bottle contained in its case, the moistened stopper inserted, covered over with the black velvet or cloth, and shaken continuously till the chloride has clotted and the liquid becomes clear ; the stopper is then slightly lifted, and its point touched against the neck

of the bottle to remove excess of liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then brought under the decimal salt burette, and $\frac{1}{2}$ c.c. added, the mixture shaken, cleared, another $\frac{1}{2}$ c.c. put in, and the bottle lifted partly out of its case to see if the precipitate is considerable; lastly, 2 or 3 drops only of the solution are added at a time until no further opacity is produced by the final drop. Suppose, for instance, that in titrating the salt solution it is found that 1.003 gm. silver require 100 c.c. concentrated, and 4 c.c. decimal solution, altogether equal to 100.4 c.c. concentrated, then—

$$1.003 \text{ silver} : 100.4 \text{ salt} :: 1.000 : x \quad x = 100.0999.$$

The result is within $\frac{1}{100000}$ of 100.1, which is near enough for the purpose, and may be more conveniently used. The operator, therefore, knows that 100.1 c.c. of the concentrated salt solution at 16° C., will exactly precipitate 1 gm. silver, and calculates accordingly in his examination of alloys.

In the assay of coin and plate of the English standard, namely, 11.1 silver and 0.9 copper, the weight corresponding to 1 gm. silver is 1.081 gm., therefore, in examining this alloy 1.085 gm. may be weighed.

When the quantity of silver is not approximately known, a preliminary analysis is necessary, which is best made by dissolving $\frac{1}{2}$ or 1 gm. of the alloy in nitric acid, and precipitating very carefully with the concentrated salt solution from a $\frac{1}{10}$ c.c. burette. Suppose that in this manner 1 gm. of alloy required 45 c.c. salt solution,

$$100.1 \text{ salt} : 1.000 \text{ silver} :: 45 : x \quad x = 0.4495, \text{ and again} \\ 0.4495 : 1 :: 1.003 : x = 2.231.$$

2.231 gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

Assaying on the Grain System.

It will be readily seen that the process just described may quite as conveniently be arranged on the grain system by substituting 10 grains of silver as the unit in place of the gramme, each decem of concentrated salt solution would then be equal to $\frac{1}{10}$ th grain of silver, and each decem of decimal solution to $\frac{1}{1000}$ th grain.

CYANOGEN.

CN = 26.

1 c.c. or 1 dm.	$\frac{N}{10}$	silver solution	= 0.0052 gm. or 0.052 grn. Cyanogen.
"	"	"	= 0.0054 gm. or 0.054 grn. Hydrocyanic acid.
"	"	"	= 0.01302 gm. or 0.1302 grn. Potassic cyanide.
"	$\frac{N}{10}$	iodine	= 0.003255 gm. or 0.03255 grn. Potassic cyanide.

1. Liebig's Method.

§ 76. THIS ready and beautiful method of estimating cyanogen in prussic acid, alkaline cyanides, &c., was discovered by Liebig, and is fully described in the "Ann. der Chemie und Pharm.," vol. lxxvii. p. 102. It is based on the fact, that when a solution of silver nitrate is added to an alkaline solution containing cyanogen, with constant stirring, no permanent precipitate of silver cyanide occurs until all the cyanogen has combined with the alkali and the silver, to form a soluble double salt; (in the presence of potash, for example, KCy, AgCy.) If the slightest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of silver cyanide occurs, the double compound being destroyed. If, therefore, the silver solution is of known strength, the quantity of cyanogen present is easily found; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination, that, when sodic chloride is present, no permanent precipitate of silver chloride occurs until the quantity of silver necessary to form the compound is slightly overstepped.

In all cases the solution to be titrated must be rendered alkaline, if not already so. Essential oil of bitter almonds, or its spirituous solution, need generally the addition of a quantity of strong spirit to prevent turbidity, from the separation of the essential oil, which would otherwise interfere with the delicacy of the reaction.

When no alkali is present, it is still possible to titrate a solution containing cyanogen with silver; but in this case the precipitate of silver cyanide appears at once, and double as much silver is required as when alkali is present. When the titration is conducted in this manner, the manipulations are precisely the same as with the deter-

mination of chlorine by silver, the silver solution being added, with constant shaking, until no further precipitate occurs. Liebig's method is, however, preferable.

Example with hydrocyanic acid: In order that each c.c. or dm. of $\frac{N}{10}$ silver solution should represent 1 per cent. of anhydrous acid, it would be necessary to take 0.54 c.c. or dm. for the analysis, but this is too little to measure with accuracy, it is better to take ten times this quantity = 5.4 c.c. or dm.; if the number of c.c. or dm. of silver solution required to produce the turbidity be divided by 10, or the decimal point moved one place to the left, the figures will represent the percentage of real prussic acid present.

5.4 c.c., therefore, of the so-called Scheele's hydrocyanic acid was carefully taken with a pipette, mixed with a small quantity of solution of potash, and titrated with $\frac{N}{10}$ silver, of which 42.5 c.c. were required; the quantity of real acid contained in the sample was 4.25%.

5.4 dm. of the *Acid. Hydrocy. dil. P. L.* were titrated as above and 19 dm. $\frac{N}{10}$ silver required = 1.9%.

54 dm. *Aq. Lauro Cerasi* titrated as above required 9.5 dm., the strength was therefore 0.095%, the decimal point being removed two places to the left, as 100 times the quantity was taken.

Caution.—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with silver nitrate, into the upper end, so as to avoid the danger of inhaling any of the acid, otherwise it is decidedly preferable to weigh it.

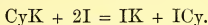
Example with potassic cyanide: The quantity of this substance necessary to be taken for analysis, so that each c.c. or dm. shall be equal to 1 per cent. of the pure cyanide, is 1.30 gm. or 13.0 grn.; 13 grains, therefore, of the commercial article were dissolved in water, no further alkali being necessary, and 54 dm. $\frac{N}{10}$ silver required to produce the permanent turbidity; the sample, therefore, contained 54% of real cyanide.

The large quantities of this material used at the present time in electro-plating and photography render it frequently desirable to ascertain its chemical strength.

2. Method of Fordos and Gelis.

This process, which is principally applicable to alkaline cyanides, depends on the fact that when a solution of iodine is added to one of potassic cyanide the iodine loses its colour so long as any unde-

composed cyanide remains. The reaction may be expressed by the following formula :—



Therefore, 2 at. iodine represent 1 at. cyanogen in combination ; so that 1 c.c. of $\frac{\text{N}}{10}$ iodine expresses the half of $\frac{1}{100000}$ at. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonated alkalis, which would equally destroy the colour of the iodine as the cyanide, consequently these must be converted into bicarbonates, best done by adding carbonic acid water (ordinary soda water).

Example: 5 gm. potassic cyanide were weighed and dissolved in 500 c.c. water, then 10 c.c. (= 0.1 gm. cyanide) taken with a pipette, diluted with about $\frac{1}{4}$ litre of water, 100 c.c. of soda water added, then $\frac{\text{N}}{10}$ iodine delivered from the burette until the solution possessed a slight but permanent yellow colour, 25.5 c.c. were required, which multiplied by 0.003255 gave 0.08300 gm., instead of 0.1 gm. or 83% real cyanide.

INDIGO.

§ 77. THIS substance, as met with commercially, is of very variable composition, and a great many processes have been from time to time proposed for estimating the amount of pure indigotin or blue matter present. These processes have for the most part been based upon experiments made with the pure material, and their accuracy has totally disappeared when used upon material containing other vegetable or earthy matters, such as are constantly to be found in marketable indigo.

These impurities are mainly indigo-gluten, indigo-brown, indigo-red, and ferric oxide, which latter would be found of course in the ash.

The volumetric processes here given are such as have been found to give the most reliable results, and may be depended upon for technical purposes. In both processes the sample is to be dissolved in fuming sulphuric acid previous to being titrated.

This is best done as follows :—1 gm. or 10 grn. respectively of the very finely powdered indigo is put into a closely stoppered small flask, or bottle, with 8 gm. or 80 grn. of acid (the relation being in each case 1 to 8), together with about a teaspoonful of small garnets, or if these are not at hand, flint pebbles or broken hard glass, the flask closely stoppered and kept for 8 or 10 hours in a warm place

not exceeding 50° C. with frequent shaking ; the sample is then ready for examination by either of the following processes :—

1. M'Kinlay's Method.

10 grns. of the indigo dissolved as described above is placed in a white porcelain basin capable of holding about two pints, and diluted with one pint of water, the bottle being repeatedly washed out with water so as to remove all colour from the garnets or glass. 50–60 grs. of oxalic acid are then added, previously dissolved in a few ounces of water ; the whole may now be diluted to about 30 fluid ounces, and is ready for titration.

Standard Potassic Bichromate, containing 60 grs. bichromate in 1000 dm. of water, each dm. of this solution equals 1 per cent. of pure indigotin.

The same solution can of course be made on the gramme system by dissolving 6 gm. bichromate in 1 litre of water, so that when 1 gm. indigo is taken for analysis, 1 c.c. bichromate will also equal 1% pure indigo blue.

The titration is now performed by running the bichromate into the indigo mixture with frequent stirring until no blue or green colour can be seen on placing a drop of the mixture on white filtering paper.

In adding the chrome solution to the blue liquor, and particularly towards the end of the process, time must be given for each addition to produce its effect before a further quantity is poured in. When the operation is finished, the mixture will present an olive green appearance, which, on standing a few minutes, will change to a golden brown. The last traces of the blue colour are best seen by drying the paper and examining it by transmitted light, but a little experience will enable an unpractised eye to judge by the appearance of the liquid ; or if any uncertainty prevails, a small quantity of the mixture may be taken out into a test-glass, and a drop of the reagent added, when, by comparing it with another portion in a similar glass, it will be seen whether any of the blue colour remains.

When the brown colouring matter of the indigo interferes with the purposes to which it is to be applied, 10 grains should be dissolved in sulphuric acid in the usual manner, and the solution being made up to 1 pint, slips of stout blotting-paper are introduced into the blue liquid, and kept therein for ten minutes, and then dried. By subjecting indigo of known strength and purity to the same treatment, and comparing the results, it will be seen that those

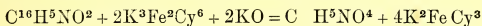
indigoes which contain a large proportion of brown matter give a green tint to the paper, varying in intensity according to the amount present.

This method has the advantage of being conducted without the application of heat, and of giving lower results than the ordinary chrome process, especially when operating with inferior qualities of indigo.

From experiments made with pure indigo, the amount of bi-chromate required to decolorise the blue solution is less when oxalic acid is employed than when hydrochloric acid with heat is used.

2. Ullgren's Process.

This is based upon the fact that red potassic prussiate destroys the blue colour of indigo in the presence of free alkali, by converting it into isatin, the reaction being formulated as follows :—



The use of caustic soda or potash, however, is liable to cause a different reaction if used in varying quantity, and at higher temperature ; it is therefore advisable to use sodic carbonate as the alkali.

Ullgren's description is as follows (Chem. Soc. Jour. 1865, 223) :—

1. The quantity of sulphuric acid added to the solution of indigo should not be too great, and the temperature must not exceed 50°, because, especially with impurer sorts of indigo, sulphurous acid in considerable quantity is then generated, and combinations with sulphuric acid are obtained, part of which are not dissolved in the acid liquid when diluted with water, like sulphopurpuric acid.

The quantity of sulphuric acid that I have found most suitable, is ten times the weight of the indigotin and eight times that of the indigo, the acid itself being of the strength which *is obtained when fuming sulphuric acid is mixed with distilled water until the mixture only is faintly fuming*. With this strength of acid the formation of a certain portion of sulphopurpuric acid is of less consequence ; only in measuring for titration, the diluted liquid must be well shaken.

2. *The indigo solution should be very much diluted*, and a sample preserved in order to serve as a guide as to the degree of dilution. To prepare the standard solution, 1 gm. of pure indigotin is dissolved in 10 gm. of sulphuric acid, mixed with water to 1 litre of liquid, and 10 c.c. of the solution thus obtained is also diluted to

1 litre of liquid ; in this there are, consequently, 10 milligrammes of indigotin dissolved. The solution of indigotin to be tested should be so much diluted that it may be lighter than this sample-coloured solution.

3. *The solution of sodic carbonate* should be saturated in the cold. 20 c.c. of this solution is mixed with the quantity of indigo solution which has been measured and afterwards diluted to be titrated ; it is so proportioned that its value of indigotin is about 10 milligrammes, but rather below than above this quantity.

4. *The solution of potassic ferricyanide* should also be very dilute. If 5.023 gm. of this salt is dissolved in 1 litre of water, then, with a certain quantity of sodic oxide, 1 c.c. of this solution destroys 1 milligramme of indigotin. But if sodic carbonate is used in corresponding quantity, another reaction takes place, in consequence of which nearly a double quantity of ferricyanide is required. This, however, is of no consequence in practice, provided we know *how much* of a solution of ferricyanide of given strength is required to destroy 1 milligramme of indigotin in solution, rendered alkaline by sodic carbonate. The solution of ferricyanide used in my experiments contained 2.5115 gm. of that salt in a litre, consequently 2 c.c. of it would just have changed 1 milligramme of indigotin into isatin.

5. When sodic carbonate is used, and the liquid is diluted to the degree above mentioned, *the change of colour* is shown in such a way that the blue colour gradually disappears, without distinctly changing into green, as is the case when the dilution is less. When the liquid has assumed a grey-yellow appearance, or generally when every tint of blue has disappeared, the operation may be regarded as complete.

The titration should be done slowly and with frequent stirring by a glass rod, and this is most easily done if the liquid is poured into a large porcelain basin, where also the change of colour can be most distinctly observed.

As an example of the applicability of the method, I will here describe a few results :—1 gm. pure indigotin was dissolved in 10 gm. of sulphuric acid, and the solution was diluted to 1 litre ; 10 c.c. of this mixed in a porcelain vessel, with 1 litre of water and 20 c.c. of a cold saturated solution of sodic carbonate, required, at a temperature of 18°, in four experiments, of the solution of ferro-cyanide : 34.5, 35.35, 35.5 c.c. : mean 35 c.c.

1 gm. Bengal indigo, No. 1, which in the reduction, partly with

grape-sugar, partly with ferrous sulphate and soda, was found to yield in even numbers 62 per cent. of indigotin, was dissolved in 8 gm. of sulphuric acid, and diluted with water to 1 litre; 10 c.c. of this mixed with $\frac{3}{4}$ litre of water and 20 c.c. of a solution of sodic carbonate saturated in the cold, required at a temperature of 18° , in four experiments, 23, 22, 22.5 and 23 c.c. of the solution of ferrocyanide of potassium: mean 22.6 c.c. But $35 : 22.6 = 100 : x = 64.4$ per cent. indigotin, consequently 2.4 per cent. more than was shown by reduction.

Similar approximate results, with 2 to 4 per cent. excess over those from the method of reduction, were obtained in experiments with several other kinds of indigo.

PART VI.

SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO COMPLETE QUANTITATIVE ANALYSIS.

ANALYSIS OF URINE.

§ 78. THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately however the most important matters, such as urea, uric acid, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, and others, during the last few years, have resulted in a truer knowledge of this important secretion, and to the two first mentioned chemists we are mainly indebted for the simplest and most reliable methods of estimating its constituents. With the relation which the proportion of these constituents bear to health or disease, the present treatise has nothing to do, its aim being simply to point out the readiest and most reliable methods of determining them quantitatively. Their pathological importance is very fully treated by some of the authorities just mentioned, among the works of which Neubauer and Vogel's "*Analyse des Harns*," (translated by the New Cavendish Society), and Prof. Lionel Beale's "*Urine, Urinary Deposits, and Calculi*," second edition, are most prominent and exhaustive.

The grain system of weights and measures will be adopted throughout this section, as being more readily applicable by medical men, while those who desire to use the gramme system will have no difficulty in working, when once the simple relation between them is understood, see § 9, p. 19.* The question of weights and measures is,

* In a word, whenever dm. occurs, c.c. may be substituted; and in case of using grammes for grains, move the decimal point one place to the left—thus 70 grains would be changed to 7.0 grammes. Of course it is understood that where grammes are taken, c.c. must be measured, and with grains dm.; the standard solution being the same for both systems.

however, of very little consequence, if the analyst considers that he is dealing with relative parts or proportions only, and as urine is generally described as containing so many parts of urea, chlorides, or phosphates, per 1000, the absolute weight may be left out of the question. The grain system, however, is more readily calculated into English ounces and pints, and therefore is generally more familiar to the medical profession of this country.

One thing, however, is necessary as a preliminary to the examination of urine, and which has not generally been sufficiently considered, that is to say, the relation between the quantity of secretion passed in a given time, and the amount of solid matters found in it by analysis. In a medical point of view, it is a mere waste of time, generally speaking, to estimate the constituents in half a pint or so of urine, passed at any particular hour of the day or night, without ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during, say 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; besides this, the analyst should register the colour, peculiarity of smell, if any, consistence, presence or absence of a deposit (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination), and lastly, its reaction to litmus should be observed.

1. Specific Gravity.

This is best taken by measuring 100 dm. into an accurately tared beaker or flask, the increase of weight in grains will be the spec. grav., water being 1000. 50 or 25 dm. may be taken instead of 100, in which case the weight multiplied by 2 or 4 will be the spec. grav. Where an accurate balance or weights are not at hand, a good urinometer may be used.

2. Estimation of Chlorides (calculated as Sodid Chloride).

This may be done in two ways, viz. :—

a. By Silver (Mohr). 10 dm. of the urine are measured into a thin porcelain or platinum capsule, and 15 grains of nitrate of potash in powder added; the whole is then evaporated to dryness, and gradually heated till the residue becomes white; it is then dissolved in a small quantity of water, and the potassic carbonate, produced by the combustion of the organic matter, *nearly* neutralised by dilute nitric acid; two or three drops of solution of potassic chromate are then added, and the mixture titrated with $\frac{N}{10}$ silver, as in § 35. 2. Each dm. of silver solution represents 0.05846 grn.

salt, consequently if 12.5 dm. have been used, the weight of salt in the 10 dm. of urine is 0.73075 grn., and as 10 dm. only was taken, the weight multiplied by 10, or what amounts to the same thing, the decimal point moved one place to the right, gives 7.3075 grains of salt for 1000 of urine.

In order to save calculation, it is convenient to measure 5.9 dm. of the urine, add about 10 grains of nitrate of potash, then evaporate, ignite, and titrate, as before directed; the number of decems of $\frac{N}{10}$ silver used will represent the number of grains of salt in 1000 grains of urine.

Example: 5.9 dm. of urine passed by a patient suffering from *Diabetes insipidus* was evaporated and titrated as above, requiring 3.1 dm. silver solution, the proportion of salt was therefore 3.1 grn. per 1000 of urine.

Where the quantity of chlorides is small, it may be advisable to use larger quantities of urine, say 58.5 dm.; in that case one-tenth of the number of dm. of silver solution required will be the number of grains of salt per 1000 urine.

Destruction of the organic matter by potassic permanganate.

Pibram (Vierteljahrsh f pract Heilk, 106, 101) obviates the necessity for evaporating the urine with potassic nitrate previous to titration by heating the urine with permanganate. 10 dm. urine are mixed with about 5 dm. $\frac{N}{10}$ permanganate, § 27, and 40 dm. water, then brought nearly to boiling; by this means a brown flocculent precipitate is produced, consisting of organic matter and manganous salt, which is filtered away, leaving the clear liquid colourless, so that an excess of permanganate shows the rose tint at once; enough permanganate must be used to give this tint, which is then removed by a few drops of oxalic acid solution, avoiding an excess, and the fluid then titrated with $\frac{N}{10}$ silver solution, as before described.

b. By Mercuric Nitrate (Liebig). The principle of this method is as follows:—If a solution of mercuric nitrate, free from any excess of acid, is added to a solution of urea, a white gelatinous precipitate is produced, containing urea and mercuric oxide in the proportion of 1 eq. of the former to 4 eq. of the latter ($4 \text{ Hg O} + \text{Ur}$). When sodic chloride, however, is present in the solution, this precipitate does not occur, until all the sodic chloride is converted by double decomposition into mercuric chloride (sublimate) and sodic nitrate, the solution remaining clear; if the exact point

be overstepped, the excess of mercury immediately produces the precipitate above described, so that the urea present acts as an indicator of the end of the process. It is therefore very easy to ascertain the proportion of chlorides in any given sample of urine by this method, if the strength of the mercurial solution is known, since 1 eq. of mercuric oxide converts 1 eq. of sodic chloride into 1 eq. each of corrosive sublimate and sodic nitrate. The strength of the standard solution of mercury is best arranged as follows :—

1. *Standard Solution of Mercuric Nitrate.* It is of great importance that the solution be pure, for if the mercury from which it is made be contaminated with traces of other metals, such as bismuth, silver, or lead, they will produce a cloudiness in the liquid while under titration, which may possibly hinder the exact ending of the reaction ; therefore 184.2 grm. of the purest red oxide of mercury, or 170.6 grm. of pure metallic mercury (the former is preferable, as being easier to weigh and less likely to be impure) are put into a beaker, with a sufficiency of pure nitric acid of about 1.20 spec. grav. to dissolve them by the aid of a gentle heat ; the clear solution so obtained is evaporated on the water bath to remove any excess of free acid. When the liquid is dense and syrupy in consistence, it may be transferred to the graduated cylinder or flask and diluted to 1000 dm. (10,000 grains), 1 dm. of the solution so prepared is equal to 0.1 grm. sodic chloride, or 0.06065 grm. chlorine. If on diluting the concentrated mercurial solution a yellow precipitate of basic mercuric nitrate should form, it must be allowed to settle, the clear liquid poured off, and a few drops of nitric acid added to the precipitate to redissolve it ; the whole is then mixed and preserved for future use in a well-stoppered bottle. It is always preferable to have this precipitate formed on dilution, as it is a proof of there being no excess of acid, which would considerably interfere with the accuracy of results.*

2. *The Baryta Solution.* Before urine can be submitted to titration by the mercurial solution, it is necessary to remove the phosphoric acid, and the proper agent for this purpose is a mixture composed of 1 volume of cold saturated solution of pure barytic nitrate and 2 volumes ditto baric hydrate ; the same agent is used previous to the estimation of urea, and may be simply designated “Baryta Solution.”

3. *The Analytical Process.* 40 dm. of the clear urine are

* Too great stress cannot be laid upon having this solution free from nitric acid in the uncombined state.

mixed with 20 dm. of baryta solution, and the thick mixture poured upon a small dry filter; when sufficient clear liquid has passed through, 15 dm. = 10 dm. urine are taken with a pipette and just neutralized, if necessary, with a drop or two of nitric acid; if not alkaline, the probability is that sufficient baryta solution has not been added to precipitate all the phosphoric and sulphuric acids; this may be known by adding a drop or so of the baryta solution to the filtrate; if any precipitate is produced, it will be necessary to mix off a fresh quantity of urine with three-fourths or an equal quantity of baryta, in which case $17\frac{1}{2}$ or 20 dm. must be taken to represent 10 dm. of the urine; the excess in either case of baryta must be *cautiously* neutralized with nitric acid.

The vessel containing the fluid is then brought under a Mohr's burette containing the mercurial solution, and small portions delivered in with stirring, until a distinct permanent precipitate is produced; it may happen that a turbidity is produced from the very first drop or two, owing to slight impurities in the mercurial solution; but as this will not increase, the point when the urea precipitate appears is not difficult to determine; the volume of solution used is then read off and calculated for 1000 parts of urine.

Example: 15 dm. of the liquid prepared with a sample of urine, as in 3 (= 10 dm. urine) required 6.2 dm. mercurial solution, the quantity of salt present was therefore 0.62 grn., or 6.2 grn. in 1000 grains of urine.

3. Estimation of Urea (Liebig).

The combination between urea and mercuric oxide in neutral or alkaline solutions has been alluded to in the foregoing article on chlorides; it will therefore probably be only necessary to say that the determination of urea in urine is based on that reaction; and as the precipitate so produced is insoluble in water or weak alkaline solutions, it is only necessary to prepare a standard solution of mercury of convenient strength, and to find an indicator by which to detect the point when all the urea has entered into combination with the mercury, and the latter slightly predominates. This indicator is sodic carbonate. If, in the course of adding the mercurial solution from the burette to the urine, a drop of the mixture be taken from time to time and brought in contact with a few drops of solution of sodic carbonate on a glass plate, slab, or watch glass, no change of colour is produced at the point of contact until the free urea is all removed; when this is the case, and the mercury is

slightly in excess, a yellow colour is produced, owing to the formation of hydrated mercuric oxide.

The compound of urea and mercury consists, according to Liebig's analysis, of 1 eq. of the former to 4 of the latter, that is to say, if the nitric acid set free by the mixture is neutralised from time to time with sodic carbonate or other suitable alkali. If this be not done, the precipitate first formed alters in character, and eventually consists only of 3 eq. of mercury with 1 of urea. In order to produce the yellow colour with sodic carbonate, there must be an excess of mercurial solution; theoretically, 100 parts of urea should require 720 parts of mercuric oxide; but practically, 772 parts of the latter are necessary to remove all the urea, and at the same time show the yellow colour with alkali, consequently the solution of nitrate of mercury must be of empirical strength, in order to give reliable results.

1. Preparation of the Standard Solution. 772 grains of red mercuric oxide, or 715 grains of the metal itself, are treated with nitric acid, as described in the article on chlorides, 2, *b* 1, and in either case diluted to 1000 dm. (10,000 grains), 1 dm. of the solution is then equal to 0.1 grn. urea. (The extreme care required to remove traces of foreign metals from the mercury is not so necessary here as in the foregoing instance, but no amount of free acid must be present.)

2. The Analytical Process. Two volumes of the urine are mixed with one of baryta solution, as before described in 2, *b* 3, of this section (reserving the precipitate for the determination of phosphoric acid, if necessary), and 15 dm. = 10 dm. urine, taken in a small beaker for titration; it is brought under the burette containing the mercurial solution (without neutralising the excess of baryta, as in the case of chlorides), and the solution added in small quantities so long as a distinct precipitate is seen to form; a plate of glass laid over dark paper is previously sprinkled with a few drops of solution of sodic carbonate, and a drop of the mixture must be brought from time to time, by means of a small glass rod, in contact with the soda; so long as the colour remains white, free urea is present in the mixture; when the yellow colour is distinctly apparent, the addition of mercury is discontinued, and the quantity used calculated for the amount of urea. It is always advisable to repeat the analysis, taking the first titration as a guide for a more accurate estimation by the second.

Example: 15 dm. of urine deprived of phosphates = 10 dm. of the original urine was titrated as described, and required 17.6 dm.

of mercurial solution ; consequently there was 1.76 grn. urea present in the 10 dm., or 17.6 grains in the 1000 of urine.

3. Corrections and Modifications. In certain cases the results obtained by the above method are not strictly correct, owing to the variable state of dilution of the liquids. The errors are, however, generally so slight as not to need correction. Without entering into a full description of their origin, I shall simply record the facts, and give the modifications necessary to be made where thought desirable.

a. The Urine contains more than 2 per cent. of Urea, *i.e.*, more than 20 grains per 1000. This quantity of urea would necessitate 20 dm. of mercurial solution for 10 dm. of urine ; all that is necessary to be done when the first titration has shown that over 2% is present is to add half as much water to the urine in the second titration as has been needed of the mercurial solution above 20 dm. Suppose that 28 dm. have been used at first, the excess is 8 dm., therefore 4 dm. of water is added to the fluid before the second experiment is made.

b. The Urine contains less than 2% of Urea. In this case, for every 4 dm. of mercurial solution less than 20, 0.1 dm. must be deducted, before calculating the quantity of urea ; so that if 16 dm. have been required to produce the yellow colour with 10 dm. urine, 15.9 is to be considered the correct quantity.

c. The Urine contains more than 1% of Sodid Chloride, *i.e.*, more than 10 grs. per 1000. In this case 2 dm. must be deducted from the quantity of mercurial solution actually required to produce the yellow colour, with 10 dm. urine.

d. The Urine contains Albumen. In this case 50 dm. of the urine are boiled with 2 drops of strong acetic acid to coagulate the albumen, the precipitate allowed to settle thoroughly, and 30 dm. of the clear liquid mixed with 15 dm. baryta solution, filtered, and titrated for both chlorides and urea, as previously described.

e. The Urine contains Ammonic Carbonate. The presence of this substance is brought about by the decomposition of urea, and it may sometimes be of interest to know the quantity thus produced, so as to calculate it into urea.

As its presence interferes with the correct estimation of urea direct, by mercurial solution, a portion of the urine is precipitated with baryta as usual, and a quantity, representing 10 dm. urine, evaporated to dryness in the water-bath to expel the ammonia, the residue then dissolved in a little water, and the urea estimated in

the ordinary way. On the other hand, 50 or 100 dm. of the urine, not precipitated with baryta, is titrated with normal sulphuric acid and litmus paper (see), each dm., of acid representing 0.17 grn. ammonia, or 0.30 grn. urea.

4. Titration of the Mercurial Solutions.

Properly speaking, no standard solutions should be used for analysis without being first titrated to ascertain their exact chemical power and to guard against accidental errors. However pure the substances from which they are made may be thought to be, it sometimes occurs that the solutions do not strictly bear the proper strength; it may also happen that absolutely pure materials are not at hand, in which case ordinary kinds may sometimes be used, if the solutions made from them be tested by experiment. In the present case, should neither pure mercury nor its oxide be obtainable, the commercial metal may be dissolved in nitric acid, the solution boiled to expel all excess of the latter, then set aside that crystals of mercurous nitrate may form; these are carefully separated from the mother liquor by draining in a funnel lightly stuffed with cotton wool, washed with cold water, then dissolved and digested in a small quantity of warm nitric acid, diluted to a certain extent with water, and a measured portion titrated for the quantity of mercury by the following process devised by Liebig, which is also applicable to the estimation of mercuric oxide for some other purposes.

The principle of the process depends on the fact that sodic phosphate precipitates mercuric phosphate from a solution of pernitrate, but not from perchloride of that metal; if, therefore, the solution containing the precipitate of mercuric phosphate produced in the first case be treated with a solution of sodic chloride, the precipitate will disappear, from the circumstance that mercuric chloride (sublimite) and sodic phosphate are formed, which both remain in solution. Consequently, if the strength of the solution of salt is known, the quantity of mercury is easily found, since 1 eq. of salt represents 1 eq. of mercuric oxide (in the form of phosphate). It is necessary, however, that directly the mercury is precipitated by the sodic phosphate the sodic chloride be added, otherwise the precipitate of phosphate becomes crystalline, and is not so readily decomposed by the salt.

The salt solution may conveniently be decinormal, § 34. 2, containing 58.46 grn. to 100 dm.—each dm. represents 0.108 grn. HgO .

The solution of sodic phosphate is simply saturated at ordinary temperature.

Process: 10 dm. of the mercurial solution, not too concentrated, are measured into a beaker; 4 dm. of the sodic phosphate solution added, and the mixture *immediately* brought under the burette containing the solution of salt, which is added carefully, with constant stirring, until the precipitate just disappears. Suppose that 18.2 dm. have been required, that number multiplied by 0.108 will give 1.9656 grn. HgO in the 10 dm. solution; but the mercurial solution for determination of chlorides requires 1.842 grn. in the 10 dm.; therefore, by a rule-of-three calculation, 9.3 dm. of this particular solution must be diluted to 10 dm. with water, to be of the proper strength, or 930 dm. to 1000 dm.

The results so obtained are not, however, strictly correct, owing to the fact that a slight excess of salt is always necessary to redissolve the precipitate. If the process be reversed, the same objection applies, since an excess of mercury is necessary to produce a permanent precipitate.

The exact point, however, is reached by combining the two methods. For instance:—

Method 1. 10 dm. of mercurial solution, with 4 dm. of sodic phosphate, are titrated with salt solution, and require 12.5 dm.

Method 2. 12.5 dm. of the same salt solution, as in 1, are measured; 4 dm. sodic phosphate added, and titrated with the mercurial solution, of which 10.25 dm. shall be required.

The following calculation will give the true power of the solutions—

1. 10 dm. mercury	=	12.5 dm. salt
2. 10.25 dm. „	=	12.5 „
<hr/> 20.25 dm. „	therefore	<hr/> 25.0 „

As the strength of the salt solution is known, the quantity of mercury contained in the 20.25 dm. is readily ascertained by a little calculation.

5. Estimation of Phosphoric Acid.—See also § 72.

This method is based on the fact that when a solution of nitrate or uranic acetate is added to a fluid containing phosphoric acid, sodic acetate, and free acetic acid, the whole of the phosphoric acid is thrown down as uranic phosphate, having a light lemon colour, and the composition $2(\text{Ur}^2 \text{O}^3)$, $\text{P}^2\text{O}^5 + \text{Aq.}$ The point at which all the phosphoric acid is precipitated may be readily ascertained by bringing a drop of the yellow liquid in which the precipitate is

suspended in contact with a drop of solution of yellow potassic prussiate on a white porcelain plate; an excess of uranic solution immediately produces a brown colour at the point of contact. The yellow precipitate is quite insoluble in acetic acid, but readily so in any of the mineral acids; therefore if any of them should be used to bring the phosphates into solution they must be neutralised by an alkali previously to adding the acetic acid and testing with the uranium solution. See fuller details in § 72.

The following solutions are required:—

1. Standard uranic nitrate, containing 406 grn. of uranic sesqui-oxide, or 709·9 grn. of uranic nitrate in 10,000 grn. of liquid. Each dm. equals 0·1 grn. $P^{2}O^{5}$. This solution cannot well be prepared by weighing the oxide of nitrate direct and dissolving, owing to the difficulty in obtaining the substances absolutely pure or with definite proportions of water in them. It is therefore necessary to graduate it by testing, as will be hereafter described.

2. Standard sodic phosphate, containing 504 grn. per 10,000 grn. Each dm. equals 0·1 grn. $P^{2}O^{5}$.

3. Solution of sodic acetate with free acetic acid to be added to urine in the proportion of 5 dm. to every 50 dm., prepared by dissolving 1000 grn. of sodic acetate in about 900 dm. of distilled water, and making up the solution to 1000 dm. with concentrated acetic acid.

4. A solution of yellow potassic prussiate, about 1 part to 20 of water, or some finely powdered prussiate.

Preparation of the Standard Solutions.

Pure uranic nitrate is dissolved in distilled water in the proportion of about 36 grn. to the ounce, and the clear solution then tested by the standard solution of sodic phosphate, in order to find its exact strength; to this end 504 grn. of pure sodic phosphate are weighed, dissolved in water, and the solution made up to 1000 dm. Each decem of such solution will contain 0·1 grn. $P^{2}O^{5}$. The plan of procedure will then be as follows: The uranium liquid of unknown strength is brought into the burette, and 10 dm. of the phosphate solution placed in a beaker together with 5 dm. of the solution of sodic super-acetate. The whole is then diluted to about 50 dm. with distilled water, and heated in a water-bath or by a spirit-lamp until somewhat hotter than it can be borne by the hand. The beaker is then brought under the burette, and the uranium solution gradually added, while a distinct precipitate is seen to form. A drop of the

mixture is then removed by a glass rod and placed upon a clean white porcelain slab or plate, and a very small drop of solution of potassic ferrocyanide solution brought by the aid of a thin glass rod into the middle of it. If no brown colour is produced, the uranium must be added drop by drop, until a faint indication occurs. The process is then repeated, and if the two trials agree, it may be considered that the strength of the solution is defined. The burette is then read off, which we will suppose to be 8.5 dm., consequently every 8½ dm. of that particular solution will need the addition of 1½ dm. of water to constitute it of such a strength that 1 dm. will represent 0.1 grn. $P^{2}O^{5}$. By the aid of a graduated glass jar, the whole of the solution may be diluted at once, the quantity of water necessary being readily ascertained for any given measure of uranium solution by a simple rule of three sum. Thus supposing there are exactly 560 dm. of solution, then $8.5 : 10 :: 560 : x = 659$. If, therefore, the 560 dm. be diluted up to 659 dm., the solution will be correct.

The Analysis.

50 dm. of the clear urine are measured into a small beaker, together with 5 dm. of the solution of sodic acetate. The mixture is then warmed in the water bath, or otherwise, and the uranium solution delivered in from the burette, with constant stirring, as long as a precipitate is seen to occur; a small portion of the mixture is then removed with a glass rod, and tested as before described; so long as no brown colour is produced, the addition of uranium may be continued; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed; if it coincides with the original testing of the uranium solution with a similar quantity of fluid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 dm. of urine; if the uranium has been used accidentally in too great quantity, 10 or 20 dm. of the same urine may be added, and the testing concluded more cautiously. Suppose, for example, that the solution has been added in the right proportion, and 9.6 dm. used, the 50 dm. will have contained 0.96 grn. phosphoric acid. With care and some little practice the results are very satisfactory.

Earthy Phosphates.

The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200

dm. of the urine are measured into a beaker, and rendered freely alkaline with ammonia; the vessel is then set aside for ten or twelve hours, for the precipitate of earthy phosphates to settle; the clear fluid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water; a hole is then made in the filter and the precipitate washed through, the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid, some sodic acetate added, and the mixture titrated as before described; the quantity of phosphoric acid so found is deducted from the total previously estimated, and the remainder gives the quantity existing in combination with alkalies.

6. Estimation of the Sulphuric Acid.

Preparation of the solution. A quantity of crystallised baric chloride is to be powdered, and dried between folds of blotting-paper. Of this, 305 grns. are dissolved in distilled water, and the liquid made up to 1000 dm. 1 dm. = 0.1 grn. SO^3 .

A dilute solution of *sodic sulphate* is also required.

The Analysis.

100 dm. of the urine are poured into a beaker, a little hydrochloric acid added, and the whole placed on a small sand-bath, to which heat is applied. When the solution boils, the baric chloride is allowed to flow in very gradually as long as the precipitate is seen distinctly to increase. The heat is removed, and the vessel allowed to stand still, so that the precipitate may subside. Another drop or two is then added, and so on, until the whole of the SO^3 is precipitated. Much time, however, is saved by using the little apparatus represented in fig. 25. A little of the fluid is thus filtered clear, poured into a test-tube, and tested with a drop from the burette; this is afterwards returned to the beaker, and more of the test solution added, if necessary. The operation is repeated until the precipitation is complete. In order to be sure that too much of the baryta-solution has not been added, a drop of the clear fluid is added to the solution of sodic sulphate placed in a test-tube or upon a plate of black glass, see § 38. 3. If no precipitate occurs, more baryta must be added; if a slight cloudiness takes place, the analysis is finished; but if much precipitate is produced, too large a quantity of the test has been used, and the analysis must be repeated.

For instance, suppose that 18·5 dm. have been added, and there is still a slight cloudiness produced which no longer appears after the addition of another half decem, we know that between $18\frac{1}{2}$ and 19 dm. of solution have been required to precipitate the whole of the sulphuric acid present, and that accordingly the 100 dm. of urine contain between 1·85 and 1·9 grn. of SO^3 .

7. Estimation of Sugar.

This method is precisely the same as described in § 73.

Preparation of the Copper Solution.

346·4 grains of pure cupric sulphate are dissolved in about 200 dm. of water. In another vessel 1730 grains of crystallised tartrate of soda and potash (Rochelle salt) are dissolved in 480 dm. of solution of pure caustic soda sp. gr. 1·14. The two solutions are then mixed, well agitated, and diluted to 1000 dm. 1 dm. of the solution so prepared represents 0·05 grn. grape or diabetic sugar. *It must be preserved in the dark, and in well-stoppered full bottles.* It should bear heating when diluted with about four or five times its quantity of distilled water, without any precipitate taking place, and should always be submitted to this test before being used; if any does occur, it probably arises from the alkali having absorbed carbonic acid; in this case the addition of a little fresh caustic soda solution remedies the evil.

The Analytical Process.

10 dm. of the clear urine are diluted by means of a measuring flask to 200 dm. with water, and a large burette filled with the fluid; 10 dm. of the copper solution ($=\frac{1}{2}$ grn. sugar) are then measured into a white porcelain capsule, 40 dm. of distilled water added, the vessel arranged over a spirit or gas lamp under the burette, and brought to boiling; the diluted urine is then delivered in cautiously from the burette until the bluish colour has nearly disappeared. The addition of the urine must then be continued more carefully, allowing the red precipitate to subside after each addition by removing the heat, when by gently sloping the capsule, the clear liquid allows the white sides of the capsule to be seen, so that the faintest shade of blue would be at once perceptible. When the colour is all removed, the burette is read off, and the quantity of sugar in the urine calculated as follows:—

Suppose that 40 dm. of the diluted urine have been required to

reduce the 10 dm. of copper solution, that quantity will have contained 0.5, *i.e.*, $\frac{1}{2}$ grn. sugar; but, the urine being diluted 20 times, the 40 dm. represent only 2 dm. of the original urine; therefore 20 grains of it contain $\frac{1}{2}$ grn. sugar, or 25 grains per 1,000.

8. Estimation of Uric Acid.

The determination of uric acid in urine is not often considered of much consequence, there are, however, circumstances under which it is desirable, especially in urinary deposits. As the quantity present in urine is very small, it is necessary to take, say from 300 to 500 dm. for the estimation.

The urine being measured into a beaker, from 5 to 8 dm. of pure hydrochloric acid are added, the whole well mixed, covered with a glass plate, and set aside in a cool place for 24 or 30 hours; at the end of that time the uric acid will be precipitated, in small crystals, upon the bottom and sides of the beaker, the supernatant liquid is decanted, washed once with cold distilled water, then dissolved in a small quantity of pure solution of potash, diluted to 6 or 8 ounces with distilled water, acidified strongly with sulphuric acid, and titrated precisely as oxalic acid, § 27. 4, with $\frac{N}{10}$ permanganate, each dm. of which is equal to 0.075 grn. uric acid. This method is not absolutely correct, owing to the fact that with the uric acid there is always precipitated a certain amount of colouring matter of the urine, which destroys the permanganate equally with the uric acid. The method by weighing is, however, open to the same objection, beside being very troublesome, so that no advantage is gained by the latter plan. Hassall states that the normal quantity of uric acid in urine has hitherto been considerably under-estimated, and that if the urine is concentrated by evaporation before precipitating with HCl, a much larger quantity will be obtained. See *Lancet*, Feb. 1865.

9. Estimation of Lime and Magnesia.

100 dm. of the urine are precipitated with ammonia, the precipitate redissolved in acetic acid, and sufficient ammoniac oxalate added to precipitate all the lime present as oxalate; the precipitate is allowed to settle in a warm place, then the clear liquid passed through a small filter, the precipitate brought upon it, washed with hot water, the filtrate and washings set aside, then the precipitate, together with the filter, pushed through the funnel into a flask, some sulphuric acid added, the liquid freely diluted, and titrated with permanganate,

precisely as in § 57; each dm. of $\frac{N}{10}$ permanganate required represents 0.028 grn. lime.

Instead of the above method the following may be adopted :—

The precipitate of calcic oxalate, after being washed is dried, and, together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of caustic and carbonate of lime. It is then transferred to a flask by the aid of the washing bottle, and an excess of normal nitric acid delivered in with a pipette; the amount of acid, over and above what is required to saturate the lime, is found, by normal caustic alkali, precisely as described in § 19, each dm. of normal acid being equal to 0.28 grn. lime.

In examining urinary sediment or calculi for calcic oxalate, it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate, as in § 27; each dm. $\frac{N}{10}$ permanganate represents 0.064 grn. calcic oxalate.

Magnesia. The filtrate and washings from the precipitate of oxalate of lime are then made alkaline with ammonia, and set aside for 8 or 10 hours in a slightly warm place, that the magnesia may separate as double magnesian and ammoniacal phosphate; the supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranic solution, as in § 5; each dm. of solution required represents 0.0563 grn. magnesia.

10. Ammonia.

The only method hitherto applied to the determination of ammonia in urine is that of Schlösing, which consists in placing a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of titrated acid. In the course of from 24 to 36 hours, all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea being decomposed into free ammonia, when heated with alkali; there is also the uncertainty as to the completion of the process, and if the vessel be opened before the absorption is perfect, the analysis is spoiled. The following plan is recommended as in most cases suitable :—When a solution containing salts of ammonia is mixed with a measured

quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved, § 17 ; that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has left to go free. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the estimation of the original amount of ammoniacal salts. The decomposition is such that while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and as this reacts equally as alkaline as though it were free potash, it does not interfere in the slightest degree with the estimation of the original ammonia.

The following is the best method of procedure :—

100 dm. of the urine are exactly neutralised with normal alkali, as in the following article, for the estimation of free acid ; it is then put into a flask capable of holding five or six times the quantity ; 10 dm. of normal alkali added, and the whole brought to boiling, taking care that the bladders of froth which at first form do not boil over ; after a few minutes these subside, and the boiling proceeds quietly ; when all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly ; the contents then emptied into a tall beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought in contact with neutral or violet coloured litmus paper produces neither a blue nor red spot ; the number of dm. of normal acid are deducted from the 10 dm. of alkali, and the rest calculated as ammonia. 1 dm. alkali = 0.17 grn. ammonia.

Example : 100 dm. of urine were taken, and required 0.7 dm. normal alkali to saturate its free acid ; 10 dm. alkali were then added, and the mixture boiled until a piece of moistened red litmus paper was not turned blue when held in the steam ; 4.5 dm. of normal acid were afterward required to saturate the free alkali ; the quantity of ammonia was therefore equal to 5.5 dm., which multiplied by 0.17 gave 0.935 grn. in 1000 of urine.

It must be borne in mind that the plan just described is not applicable to urine which has already suffered decomposition by age or other circumstances so as to contain carbonate of ammonia ;

in this case it would be preferable to adopt Schlösing's method ; or where no other free alkali is present, direct titration with normal acid may be adopted.

11. Estimation of Free Acid.

The acidity of urine is doubtless owing to variable substances, among the most prominent of which appear to be acid sodic phosphate and lactic acid, other free organic acids are probably in many cases present ; under these circumstances, the degree of acidity cannot be placed to the account of any particular body ; nevertheless, it is frequently desirable to ascertain its amount, which is best done as follows :—

100 dm. of the urine is measured into a beaker, and normal alkali, delivered in drop by drop from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper, produces no change of colour ; the degree of acidity is then registered as being equal to the quantity of normal alkali used.

12. Estimation of Albumen.

a. By Weight. 100 dm. of the clear urine, or less than that quantity if much albumen is present, the 100 dm. being made up with water, are introduced into a good-sized beaker, and heated in the water bath for half an hour. If the urine is sufficiently acid, the albumen will be separated in flocks. Should this not be the case at the end of the half-hour's heating, and the fluid merely appears turbid, one or two drops (not more, unless the urine is alkaline) of acetic acid are added, and the heating continued until the albumen separates in flocks ; the beaker is then put aside till the precipitate has settled, and the clear liquid passed through a small filter (previously dried at 212° , then cooled between two watch glasses held together with a spring clip, and weighed) ; the precipitate is then washed with a little hot water, and brought upon the filter without loss, the beaker washed out with hot distilled water, and the last traces of precipitate loosened from the sides with a feather. The filter with its contents is then repeatedly washed with hot water, until a drop of the filtrate evaporated on a piece of glass leaves no residue. The funnel containing the filter is then put into a warm place to dry gradually ; lastly, the filter removed into one of the watch glasses and dried thoroughly in the air bath at 110° C., or 220° Fahr. ; another watch glass is then covered over that

containing the filter, the spring clip passed over to hold them together, the whole cooled under the exsiccator and weighed ; the weight of the glasses, filter, and clip deducted from the total, gives the weight of albumen in 1000 grains of urine, supposing 100 dm. has been originally taken.

b. By Measure. In order to avoid the tedious process of estimating the albumen as just described, Bödeker has devised a method of titration which gives very fair approximate results. The principle is based on the fact that potassic ferrocyanide completely precipitates albumen from an acetic acid solution in the atomic proportions of 211 ferrocyanide to 1612 albumen.

The standard solution of ferrocyanide is made by dissolving 13·09 grains of the pure salt in 10,000 grains of distilled water. 1 dm. of the solution so prepared precipitates 0·1 grn. albumen.

Process : 50 dm. of the clear filtered urine are mixed with 50 dm. of ordinary commercial acetic acid, and the fluid put into a burette. Five or six small filters are then chosen, of close texture, and put into as many funnels, then moistened with a few drops of acetic acid, and filled up with boiling water ; by this means the subsequent clear filtration of the mixture is considerably facilitated. 10 dm. of the ferrocyanide solution are then measured into a beaker, and 10 dm. of the urinary fluid from the burette added, well shaken, and poured upon filter No. 1. If the fluid which passes through is bright and clear with yellowish colour, the ferrocyanide will be in excess, and a drop of the urine added to it will produce a cloudiness. On the other hand, if not enough ferrocyanide has been added, the filtrate will be turbid, and pass through very slowly ; in this case, frequently both the ferrocyanide and the urine will produce a turbidity when added. In testing the filtrate for excess of ferrocyanide, care must be taken not to add too much of the urine, lest the precipitate of hydroferrocyanide of albumen should dissolve in the excess of albumen.

According to the result obtained from the first filter, a second trial is made, increasing the quantity of urine or ferrocyanide half or as much again, and so on until it is found that the solution first shown to be in excess is reversed ; a trial of the mean between this quantity and the previous one will bring the estimation closer, so that a final test may be decisive.

Example : 50 dm. of urine, passed by a patient suffering from Bright's disease, were mixed with the like quantity of acetic acid, and tested as follows :—

Urine.	Ferrocyanide.	Urine.	In filtrate Ferrocyanide. gave
1. 10 dm.	10 dm.	0	prec.
2. 10 „	20 „	prec.	0
3. 10 „	15 „	0	prec.
4. 10 „	17.5 „	0	faint prec.
5. 10 „	18 „	0	0

Therefore, the 10 dm. of diluted urine = 5 dm. of the original secretion, contained 1.8 grn. albumen, or 36 grains per 1000.

13. Estimation of Soda and Potash.

50 dm. urine are mixed with the same quantity of baryta solution, allowed to stand a short time, and filtered; then 80 dm. = 40 dm. urine, measured into a platinum dish and evaporated to dryness in the water-bath; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, ammoniac carbonate added so long as a precipitate occurs, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and ammoniac carbonate, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed sodic and potassic chlorides is obtained; the proportion of each is found by titrating for the chlorine, as in § 36, *h*, and calculating as there directed under the head of "mixed alkaline chlorides."

14. Estimation of Total Solid Matter.

The correct determination of the total solid matter is a very difficult task, owing to the fact that, on the one hand, the residue is very hygroscopic, and, on the other, that a partial decomposition of the urea takes place by heating it to a sufficient temperature to expel all the water. A tolerably satisfactory plan is to measure 5 dm. into a shallow platinum or porcelain capsule, which is placed beside a vessel of strong sulphuric acid, under the receiver of a powerful air-pump, and kept *in vacuo* until all moisture is removed.

A rough estimation may be made by evaporating 10 or 20 dm. of the urine on the water-bath, then drying in the air-bath at 115° C. or 230° Fahr., until the weight remains tolerably constant.

The only *correct* method is to introduce a measured portion of the urine, not more than 3 or 4 dm. (contained in a small boat-shaped capsule, filled with fragments of glass), into a wide glass tube passing through boiling water, to one end of which is attached an aspirator, to the other a chloride of calcium tube; between the aspirator and the tube containing the urine a small flask is inserted, containing a measured quantity of normal sulphuric acid, so that any ammonia, given off in the evaporation, is retained, and its quantity afterwards found by titration with normal alkali; it is then calculated into urea, and its weight added to the dry residue actually found. For further details see Neubauer's paper in the "Zeitschrift für an Chemie," part. ii. p. 166.

15. Estimation of the Total Saline Matter.

A measured portion of the urine, say 10 dm., is evaporated to dryness in a small porcelain crucible, about 10 drops of nitric acid added, and the crucible gradually heated to dull redness; it is then suffered to cool, and the same quantity of nitric acid again added; then heated up again gradually to a moderately strong heat until all the carbon is destroyed and the residue white; it is then cooled and weighed.

ANALYSIS OF SOILS.

§ 79. THE following instructions for the examination of soils are not given so much for the use of practised scientific chemists, as for the guidance of those who may not have the advantage of a complete laboratory, or who may only desire to estimate some of the principal constituents of a soil.

The instructions for mechanical analysis, the importance of which cannot be overrated, are taken from Dr Noad's article on soils in the "Chemist and Druggist."

1. Mechanical Analysis of a Soil.

a. Selection of the Sample. Too much care cannot be taken to obtain a fair average specimen. For this purpose one or two pounds should be taken from each of four or five different parts of the field where the soil appears to be nearly the same. These should be well mixed together, and a pound or so selected for analysis; all samples should be kept in well-corked bottles. It is not unfrequent to see in a field, otherwise fertile, a few patches almost barren, where plants, especially when the field is in white crop, spring up, and for a time look quite healthy, but soon become

diseased, assume a yellow colour, and die. Specimens from such parts should on no account be mixed with the rest; they should be examined by themselves, and the results compared with those given by the fertile parts; by following this course the cause of sterility and the means of curing it are most likely to be discovered.

b. Determination of Water. Spread a weighed quantity (say half a pound) of the soil upon a sheet of white paper, and expose it to the air in a dry room for several hours, weighing it at intervals of two or three hours till the weight remains constant; the loss indicates the amount of water which has evaporated, but by no means the whole of the water which the soil contains. To determine which, heat about 500 grains of the air-dried soil in a small glass beaker plunged into an oil bath, the temperature of which is kept between 150–160° C. (300°–350° Fahr.), till it ceases to lose weight, the result gives a close approximation to the amount of water. *Absolute* desiccation cannot, however, be accomplished except at a heat close upon redness, which is, of course, inadmissible, as the organic matters the soil contains would thereby become altered or destroyed.

c. Absorbing power. Allow the 500 grains of soil dried as above to cool in a covered vessel; then spread it out on a sheet of paper, and expose it to the air for 24 hours; note the increase of weight which is due to absorption of water, and if it amounts to 10 grains, it is so far an indication of great agricultural capability.

d. Power of holding water. Put 1000 grains of air-dried soil into a filter enclosed in another, placed in a funnel; pour cold water, drop by drop, on the soil until it begins to trickle down the neck of the funnel; cover with a piece of glass, and allow it to stand for an hour or two, adding a few drops of water from time to time until it is certain that the whole soil is perfectly soaked; remove the filters from the funnel, and open them upon a linen cloth to remove the drops of water adhering to the paper. The outside filter is now placed in one pan of the balance, and the inner one containing the soil on the other; and the whole being carefully balanced, the true weight of the wet soil is obtained. Suppose this to be 1400, then the soil is capable of holding 40 per cent. of water.

e. Rapidity of Drying. Expose the soil with its filter on the plate to the air for 4, 12, or 24 hours, weighing from time to time. The loss of weight, indicating the tendency of the soil to dry, may convey useful information as to the necessity or otherwise of drainage.

f. Relative proportions of Gravel, Sand, and Clay. Rub a quantity of air-dried soil between the hands, and remove and weigh any *stones* which may be present. Weigh off 4000 grains, and pass them through a sieve (No. 1) of copper wire gauze, the meshes of which are about $\frac{1}{16}$ th of an inch in diameter. Remove the sieve from its bottom, and place it over a deep evaporating basin; throw a gentle stream of water upon the contents, and stir with a spatula or the hand until the water passes through clear. Transfer the residue to another basin, and place it in the water-oven to dry; then weigh, after which ignite in the air, and when cold weigh again. The first weighing gives the amount of *coarse gravel*, and the second indicates the proportion of *organic matter* which this gravel contains. Transfer the soil which has passed through sieve No. 1 to sieve No. 2, the meshes of which are about $\frac{1}{8}$ th of an inch in diameter, treat the residue on the sieve precisely as before, dry at 212° , weigh, ignite, and weigh again; the results give the amount of *gravelly sand*, and of organic matter mixed with it. Dry a portion of the soil which has passed through sieve No. 2 in the water oven, and weigh off 500 grains; transfer to a deep basin or flask, and boil for 20 minutes or so with water. The boiling must be continued until all the particles are thoroughly separated from each other. The *coarse sand*, *fine sand*, and *finely divided particles* are then separated from each other by the following simple process, recommended by Schultz:—The boiled soil is allowed to cool, and is then washed into an *elutriating glass*, which is merely a tall champagne glass 7 or 8 inches deep, and about $2\frac{3}{4}$ inches wide at the mouth, round which is fastened a brass ring about half an inch broad, with a tube slightly inclined downwards proceeding from its side. A gentle stream of water is caused to pass continuously into the elutriating glass in such a manner as to cause a constant agitation of the particles, whereby the finest are washed away through the tube at the top of the glass, and received in a beaker or any other convenient vessel. This stream of water is best kept up and regulated by causing it to flow from a reservoir provided with a stop-cock, to which is attached a tube funnel from 12 to 18 inches long, drawn out to a point, with a fine aperture. The end of this tube is placed nearly at the bottom of the elutriating glass, and the supply of water so adjusted that the funnel tube always remains half full of water. When the water runs off from the discharge tube nearly clear, the stop-cock of the reservoir is closed, and the elutriating glass being removed, the water is decanted

from it, and it is washed into a small dish, where it is dried and weighed, after which it is ignited and weighed again; the two weights give the proportion of *coarse sand* and its *organic matter*. The elutriated turbid fluid is allowed to stand for several hours, and the water is then poured off into another beaker. The deposited matter, consisting of *fine sand* and *fine soil*, is then subjected to a second elutriating process, conducted as before, except that the force and volume of the washing water is considerably lessened. The operation is continued until the wash water passes off quite clear; this sometimes takes three or four hours, but it is, with the arrangement described, a self-acting process, requiring no personal superintendence. The residue in the elutriating glass is *fine sand*, which, with its organic matter, is estimated as before, by drying, weighing, igniting, and re-weighing. We have only now to deduct from the original 500 grains the quantities of *coarse* and *fine sand*, to obtain the proportion of finely-divided matter. The results of this mechanical analysis may be tabulated thus (Schultz):—

100 parts of the soil, dried at 212° Fahr., contain (for example)—

		Fixed Substances.	Combustible or Volatile Substances.
6.90	{ Gravel (coarse) . . .	6.90	0.00
	{ Organic matter
7.10	{ Gravel (fine) . . .	6.43	...
	{ Organic matter	0.67
35.50	{ Sand (coarse) . . .	34.37	...
	{ Organic matter	1.13
40.00	{ Sand (fine) . . .	38.50	...
	{ Organic matter	1.50
10.50	{ Fine soil . . .	9.50	...
	{ Organic matter, ammonia, and combined water	1.00
100.00		95.70	4.3

Stones, 2.10 per cent.

This mechanical treatment of soils is of high importance, and it is to be regretted that so few of our English soils have hitherto been so examined. The same remark applies to the analysis of *clays*. The operations above described apply equally to *clays* and to *soils*, except that in the case of clays we have not to look for *gravel*.

To render the matter complete, however, the gravel and sand

should be moistened and examined under the microscope, with the view of ascertaining if they are wholly siliceous, or if they contain also fragments of different kinds of rock—sandstones, slates, granites, traps, limestones, or ironstones. A few drops of strong hydrochloric acid should also be added, when the presence of limestone is shown distinctly by an effervescence of peroxide of iron by the brown colour which the acid speedily assumes; and of black oxide of manganese by the smell of chlorine, which is easily recognised.

g. Determination of the Density of a Soil. Dry a sample of the soil (from which the large stones have been picked out) at 212° in the water oven till it ceases to lose weight. Fill a perfectly clean and dry common phial with distilled water up to a mark made with a file on the neck, and weigh it carefully. Pour out part of the water, and introduce into the bottle in its stead 1000 grains of the dried soil; shake the bottle well, to allow the air to escape from the pores of the soil; fill up again with water to the mark on the neck, and again weigh. The weight of the soil divided by the difference between the weight of the bottle with soil and water, and the sum of the weights of soil and the bottle of water together, gives the density or specific gravity. Example—

	Grains.
The bottle with water alone weighs	2000
The dry soil	1000
<hr/>	
Sum (being the weight which the bottle with the soil and water <i>would have had</i> , could the soil have been introduced without displacing any of the water)	3000
Actual weight of soil and water	2600
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Difference (being the weight of water taken out to admit 1000 grains of soil)	400

Therefore, 1000 grains of soil have the same *bulk* as 400 grains of water—*i.e.*, the soil is $2\frac{1}{2}$ times heavier than the water, since $\frac{1000}{400} = 2.5$, its specific gravity.

h. Determination of the Absolute Weight. Weigh an exact imperial half-pint of the soil in any state of dryness. When this weight is multiplied by 150 it will give very nearly the weight of a cubic foot of the soil in that state.

2. Chemical Analysis.

The accurate and complete quantitative analysis of soils is a work of some difficulty, and cannot be entirely accomplished by volumetric means. Many of the principal substances, however, may be estimated in this manner, and the following method of procedure is given as the most convenient:—

1. Water. 250 grains of the air-dried sifted soil are weighed in a porcelain, platinum, or iron crucible, and heated for a considerable time in the water bath till the weight is constant. The loss represents the amount of water.

2. Organic matter. 50 grains of the residue from 1 are ignited in a platinum or porcelain crucible until all the organic matter is destroyed; the residue is then suffered to cool, moistened with solution of carbonate of ammonia (to re-carbonate any lime), then dried in the air bath at about 150°C. , or 300°Fahr. ; the loss indicates the amount of organic matter in the perfectly dry soil, which is then calculated for 100 parts of air-dried soil.

3. Carbonic Acid. 50 gr. of the air-dried soil are introduced into the apparatus, fig. 20, and the carbonic acid estimated as in § 23.

4. Chlorine. 250 gr. of the air-dried soil are burnt in a platinum crucible, then cooled and moistened with a solution of potassic nitrate, again heated gently to dryness, then ignited again. The cold residue is then lixiviated with boiling water, filtered, the filtrate neutralised with acetic acid, and a measured portion of it titrated with $\frac{N}{10}$ silver and chromate, as in § 35. 2.

5. Oxide of Iron. The insoluble residue of 4 = 250 gr. soil, is heated in the water bath with pure hydrochloric acid to extract all soluble matter, the solution filtered off, the residue washed with boiling water on a filter (residue preserved for future examination), and the filtrate and washings collected and diluted to 500 dm.; 200 dm. = 100 gr. soil, are then taken, heated with a little nitric acid to peroxidise all the iron, and ammonia added in excess, so as to precipitate all oxide of iron and alumina; if the latter be required to be estimated, the precipitate must be collected on a filter, well washed, putting the filtrate and washings aside, then dried, ignited, and weighed; the residue, consisting of oxide of iron and alumina, with whatever traces of phosphoric acid there may be, is redissolved in a little hydrochloric acid, the solution treated with zinc, diluted considerably, and titrated with $\frac{N}{10}$ bichromate,

§ 30. 1, for oxide of iron ; the quantity so found deducted from the total weight of the precipitate gives the alumina and phosphoric acid. Should the estimation of alumina not be required, the precipitate need not be ignited, but simply redissolved with hydrochloric acid on the filter and titrated at once for iron. Should any portion of the iron in the original soil exist as protoxide, a weighed quantity, say 100 grains, of the fresh, sifted, and non-ignited soil, is exhausted with pure hydrochloric acid, the solution filtered and titrated direct with bichromate.

6. Lime. The filtrate and washings from 5 = 100 gr. soil, are mixed with ammoniac oxalate in excess, the solution set aside in a warm place for an hour or so, the precipitate then collected on a filter, well washed, dried, and together with the filter ignited. The mixture of carbonate and caustic lime thus obtained is dissolved in an excess of normal nitric acid, and titrated as in § 57 ; calculation for lime to be made as there directed.

7. Magnesia. The filtrate and washings from 6 = 100 gr. soil, which if bulky, must be evaporated somewhat in the water bath, is to be made freely alkaline with ammonia, ammoniac arsenate added in slight excess, and the solution set aside for twelve hours in the cold, that the magnesia may be precipitated as double ammoniac and magnesian arsenate. The precipitate collected on a filter well washed with ammoniacal water (filtrate and washings set aside), redissolved on the filter with acetic acid, and the solution titrated with uranium, as in § 72 ; see also 62. 4. 1 dm. of standard uranium solution represents 0.0563 grn. MgO.

8. Alkalies. The filtrate and washings from 7 = 100 gr. soil, containing the alkalies as chlorides, together with ammoniac chloride and a small quantity of ammoniac arsenate, is evaporated to dryness on the water bath, then ignited gently and carefully under a chimney to volatilise all the arsenate and other salts of ammonia. The alkalies are then left nearly pure as chlorides ; the residue is dissolved in a very little water, filtered through a small filter into a small crucible, evaporated to dryness, and weighed direct. If it be desirable to ascertain the amount of potash, it may be separated by weight as potassio-platinic chloride, or the indirect method of calculation, as in § 36, may be adopted.

9. Phosphoric Acid. The remainder of the acid solution, viz., 300 dm. = 150 gr. soil, is mixed with a little nitric acid, heated and precipitated with ammonia, as in 5, the precipitate collected on a filter and washed with boiling water (filtrate and washings set

aside); the precipitate is then dissolved on the filter with dilute nitric acid, the filter slightly washed, and the solution so obtained digested in the water bath for twenty-four hours with about two ounces of the fluid prepared as follows :—

Molybdic acid	100 grains
Solution of ammonia, '900 . . .	100 dm.
Pure nitric acid, about 1.30 . . .	150 dm.

If any precipitate occurs, it will contain all the phosphoric acid (unless it should exist in large quantity, which is not probable) as ammonic phospho-molybdate, which is to be collected on a small filter, well washed with the same fluid, then redissolved in ammonia, and a portion of the magnesia mixture added, § 72, to precipitate the phosphoric acid as double ammonio-magnesian phosphate; the precipitate so produced is dissolved in acetic acid, and titrated with uranium as in § 72.

10. Sulphuric Acid. The filtrate and washings from 9 = 150 gr. soil are diluted up to a definite measure, and a convenient portion titrated for sulphuric acid by any of the methods given in § 38.

11. Ammonia. From 200 to 500 grains of the fresh air-dried soil are introduced into the distilling flask (fig. 19), together with a little water and a small piece of bees' wax (to prevent frothing); the tube *d* is filled with strong caustic potash or soda, the whole of which is allowed to run into the flask as soon as the heating commences. In all other respects the operation is conducted as described in § 17.

12. Nitrogen. 100 grains of the soil are dried at 300° Fahr., and when cold mixed with soda lime in a combustion tube, and ignited as usual, § 80. 9. The ammonia evolved may be received into normal sulphuric acid, and the mixture afterwards titrated with normal alkali in the usual manner; or dilute hydrochloric acid may be used in the bulb apparatus, the fluid evaporated to dryness on the water bath, then heated in the air bath to 240° Fahr., and the residual ammonic chloride titrated as in § 36.

13. Residue insoluble in Hydrochloric Acid. The insoluble matter which has already been collected, as in 5 = 250 gr. soil, and consisting mainly of insoluble silicate of alumina and sand, is transferred to a platinum or porcelain dish or large crucible, dried and mixed with sulphuric acid of about 1.6 sp. gr. in excess; the mixture is left to digest somewhat, then heated slowly under a

hood, to drive off all the free acid; the residue is then cooled, lixiviated with water, filtered, and the filtrate precipitated with ammonia; the precipitate may be washed, dried, ignited, and weighed as "Alumina insoluble in hydrochloric acid." The insoluble residue will consist of pure quartz sand.

ANALYSIS OF MANURES.

1. Guano.

§ 80. 1. Moisture. 100 grains, weighed in a platinum or porcelain crucible, are dried in the water bath till the weight is constant; the loss gives the percentage of moisture. It must, however, be borne in mind that in drying guano very often a loss of ammonia takes place; this can only be avoided by drying the sample in a current of warm air by means of an aspirator, and passing the air so flowing over the surface of the guano through normal acid in a bulb tube.

2. Total Fixed Constituents. Residue of 1 = 100 grains guano are ignited at a low red heat till all organic matter is destroyed, and the residue of a white or greyish colour; the loss of weight gives the percentage of fixed constituents, which will act as a control over the subsequent analysis.

3. Sand, Clay, or other Insoluble Matter. Residue of 2 is boiled with dilute hydrochloric acid (which should not cause any amount of effervescence) till all soluble matter is extracted; the solution filtered, residue brought on the filter, washed, dried, ignited, and weighed, gives the percentage of insoluble matter. The filtrate and washings containing all the soluble matters are diluted up to a definite measure, say 500 dm.

4. Phosphoric Acid as Insoluble Phosphates.* 200 dm. of the solution prepared as in 3 = 40 grains guano are precipitated with ammonia in excess, the precipitate of phosphate of lime and magnesia redissolved in acetic acid, and the solution divided in half, one portion titrated with uranium for total phosphoric acid, as in § 72, the remainder set aside for

5. Lime. To half of the acetic acid solution prepared as in 4, sufficient oxalate of ammonia is added to precipitate all the lime; after standing an hour or so, the supernatant liquid is filtered off, and

* The amount of phosphoric acid existing as alkaline phosphates in a soluble form may be estimated separately in 1 gm. guano simply exhausted with water and titrated with uranium.

the precipitate washed (reserving the filtrate and washings), then dissolved and titrated as in § 57.

6. Magnesia. The filtrate and washings from 5 are rendered alkaline with ammonia, set aside for 12 hours, the precipitate of double phosphate of magnesia and ammonia collected, dissolved, and titrated as in § 72. See also 79. 2. 7.

7. Alkalies. The filtrate and washings from 6 are mixed with sufficient baryta water to remove all the phosphoric and sulphuric acids; the precipitate removed by filtration; the filtrate evaporated to a small bulk, and treated with carbonate and caustic ammonia, to remove excess of baryta, and the filtrate and washings from this precipitate acidified with hydrochloric acid, evaporated to dryness, ignited, then redissolved in a small quantity of water, a few drops each of ammonia and ammoniac carbonate added, filtered into a weighed platinum or porcelain crucible, the small filter thoroughly washed, and the filtrate and washings evaporated to dryness, ignited, and weighed as chlorides.

For the estimation of potash and soda contained in the mixture see § 36, which also contains rather more minute directions for the careful separation of the alkaline salts by the above method.

8. Ammonia. 10 grains of the guano, or more, if poor in ammonia, are boiled with caustic potash in the distilling apparatus, fig. 19, and the estimation of ammonia conducted as described in § 17. This gives the ready formed ammonia only.

9. Nitrogen and Ammonia. From 5 to 10 grains of the guano, according to its quality, are dried in the water bath and carefully mixed with soda lime (previously coarsely powdered, heated, and cooled), and the mixture introduced into a hard glass tube, closed at one end, about fourteen inches long and half-an-inch diameter; the closed end is previously filled to about three quarters of an inch with a dried mixture of equal parts oxalic acid and soda lime; on the top of this the mixture is placed about an inch of soda lime, then the mixture of guano and soda lime is filled in to within about two inches of the open end, and upon the top of it more plain soda lime; finally, a loose plug of dry asbestos is introduced, and a good fitting cork, carrying the Varrentrapp and Will's bulb apparatus (filled to the proper extent with normal sulphuric acid), inserted. The tube is then wrapped round with a piece of iron or copper gauze, placed in the gas or charcoal combustion furnace, and gradually heated from its open end downwards until the ammonia is nearly all evolved; the whole tube is then strongly

heated, and the heat brought especially to bear on the lower end containing the mixture of oxalic acid and soda lime ; by this means a strong current of carbonic acid is produced, which drives out all the ammonia into the acid ; when this strong current ceases somewhat, and before the acid has opportunity to regurgitate into the hot exhausted tube, the cork is removed, the acid solution emptied into a beaker, the bulbs washed out into the same vessel, the mixture filtered, if necessary, and the excess of acid ascertained by titration with normal alkali, as in § 16. Each dm. of acid found to be combined with ammonia represents 0.17 grn. of that substance, or 0.14 grn. nitrogen.

2. Raw Phosphates and Phosphatic Manures.

Moisture and fixed constituents are determined as in the case of guano.

100 grains of the manure are lixiviated repeatedly with cold water, by aid of a mortar and pestle, pouring off each washing into a beaker, allowed to settle, the clear liquid passed through a filter ; the residue boiled once or twice with water, the fluid being decanted through the same filter, the residue is then mainly brought upon it and well washed with boiling water ; the filtrate and washings so obtained are diluted to 500 dm., set aside and marked "Aqueous solution," 100 gr. manure.

The insoluble residue on the filter is pushed through the funnel into the beaker in which it was originally digested, the filter treated with warm dilute hydrochloric acid, washed with boiling water into the beaker, a good quantity of hydrochloric acid added, and the whole digested for some time at near boiling heat. The clear acid fluid is then passed through a filter, the insoluble residue brought upon it and washed till all soluble matter is removed, filtrate and washings then diluted to 500 dm., set aside and marked "Acid solution," 100 gr. manure.

The insoluble residue on the filter is dried, ignited, and weighed, as sand, clay, &c.

In the aqueous solution, lime and alkalies are determined as in the case of guano ; sulphuric acid as in § 38 ; the phosphoric acid as described further on.

In the acid solution, which contains traces of iron, and probably alumina, the phosphoric acid is separated and estimated as recommended in § 72. Lime and sulphuric as in the aqueous acid solution ; oxide of iron, if necessary, by bichromate or permanganate, as in §§ 30, 28, 27.

Ammonia and nitrogen as in guano, should the quantity be considerable ; if not, a very convenient use may be made of Nessler's solution for estimating approximately the ammonia ready formed in the manure, as follows:—1 gm. of the manure is to be distilled with 150 c.c. water and 50 c.c. solution of sodic carbonate (normal or about that strength) from a small retort arranged for estimation of ammonia in water by Wanklyn's process, § 82, by distilling 50 c.c., the whole of the ammonia will be contained therein, should there be about 1% in the manure ; by diluting this 50 c.c. of distillate to 500 c.c., and taking 100 c.c. (= 0.28 gr. manure) for comparison with standard ammonic chloride or sulphate by Nessler's test, a very near approximation may be obtained.

If the percentage of ammonia is greater than here mentioned, it will be preferable to distil into normal acid, as in § 17.

SPECIAL PROCEDURE FOR PHOSPHORIC ACID.

§ 81. In the following processes the estimation of phosphoric acid is in all cases accomplished by means of uranium, as more fully described in § 72. Those who will take the pains to work out the details attentively will find the results very reliable.

Repeated trials side by side with the gravimetric estimation of P_2O_5 , as molybdic phosphate and ammonio-magnesian phosphate, have shown the most concordant results in the hands of many well-known and expert operators, among which are Fresenius, Neubauer, Stohmann, Groeser, Kissel, &c. The chief difficulty, as applied to manures of all classes, is the separation of the phosphoric acid in such a form as to be readily and accurately estimated by the process.

In all cases it is advisable to use a solution of uranic nitrate of such strength that 1 c.c. or 1 dm. (according to the system of measures used) shall equal 1 per cent. of tricalcic phosphate (generally known as insoluble phosphate or bone earth) when 1 gm. or 10 grains respectively of the original substance is taken for analysis. By this arrangement all calculation is avoided.

1. Standard Uranic Solution.

About 35 gm. crystals of uranic nitrate are dissolved in nearly a litre of water, or 350 gm. in 1000 dm. Exact quantities are not important.

The strength of the solution must now be found exactly, and necessitates a standard solution of sodic phosphate. Some pure crystals of sodic phosphate are powdered and pressed repeatedly

between filter paper to remove all adhering moisture, and 23.1 gm. dissolved and made up to 1 litre, or on the grain system, 231 gm. to 1000 dm. The uranic solution must be made to agree with this, drop for drop. In order to titrate the strength of the uranic solution, it is necessary to have an

2. Acid Solution of Sodic Acetate.

Dissolve 100 gm. of sodic acetate in water, add 100 c.c. strong acetic acid, and make up to 1 litre with water. 1000 gm. each of acetate and acetic acid in 1000 dm. will correspond for the grain system.

Process: Measure 50 c.c. or dm. of the standard sodic phosphate into a small beaker; drop into it 5 or 6 drops of strong solution of ammonia, with a tiny piece of litmus paper (blue or red); under any circumstances it will become blue with the ammonia; then drop in acetic acid until the ammonia is neutralised, and the acetic acid is in excess, known by the litmus turning red. (There is no actual necessity for doing this in titrating with the sodic phosphate, but the reason for it is, that in the actual analysis of insoluble phosphates, they always exist in acid solution, and have to be neutralised with ammonia, and again dissolved in acetic acid before titration, and therefore it is advisable to produce artificially the same circumstances as will occur in the actual analysis, otherwise the same amount of colour in testing may not be obtained). Add 5 c.c. or dm. of sodic acetate solution, warm to about 70° C. = 150° Fahr., then run in the uranic solution from a burette cautiously, and test for the necessary reaction exactly as described in § 72.

The strength being so found, the uranic solution is diluted to the required measure, to balance the phosphate solution exactly. This precaution is especially necessary, that whatever amount of brown colour is taken as the end of the process in standardising the uranic solution, should be always taken in the actual analysis of the phosphate; and, moreover, the quantity of fluid used in the actual analysis must not greatly vary from that used in the original titration.

3. Estimation of the Soluble Phosphates in Manures (Monocalcic Phosphate).

10 gm. or 100 gr. respectively of the sample is weighed and transferred to a glass or porcelain mortar, and rubbed repeatedly with fresh portions of cold water, pouring off the milky fluid into a

1000 c.c. or dm. flask, and finally transferring all the insoluble residue from the mortar to the flask by the help of small quantities of water; the measure is then made up to exactly, and set aside, with occasional shaking for two hours at least. Where a series of samples have to be examined, one can be prepared after another, so that by the time the last is finished the first may be ready for titration. Where no great haste is needed, it is better to prepare the samples over-night. If the contents of the flask, after standing the requisite time and having been shaken, is still milky, a portion may be filtered through a dry filter into a dry vessel, and 100 c.c. equal to 1 gm. manure (or 100 dm. = 10 grn.) taken for the analysis; or the flask may be allowed to stand until all has settled and the supernatant fluid become quite clear.

In either case the measured quantity is taken out with a pipette, and solution of ammonia dropped into it cautiously until no further precipitate is produced; a great excess of ammonia must be avoided, but care must be taken that there is enough to neutralise all the free acid in the manure; strong acetic acid is then added until the ammonia is completely neutralised, which may be known by dropping in a small piece of litmus paper, and stirring well until the colour of the paper is distinctly red. If the precipitate is not completely dissolved, add about 10 or 20 drops more acetic acid, and observe whether any cloudiness still remains; if so, iron or alumina is present, and the cloudiness consists of phosphate of iron or alumina, or a mixture of both, which is insoluble in acetic acid. Should the quantity be considerable, the manure must either be analysed by a different method, or the precipitate may be filtered away from the fluid on a small filter, washed with hot water, dried, ignited, and weighed as phosphate of alumina. The filtrate and washings can then be evaporated to about the same bulk as at first, and the monocalcic phosphate estimated by titration with the uranic solution. We will suppose, however, as is generally the case, that there is none, or only a very small quantity, of iron or alumina present, and that the fluid, after acidifying with acetic acid, is clear, or nearly so. Add 5 c.c. of sodic acetate solution, heat to near boiling in the water-bath or over a flame, and proceed to titrate with the uranic solution as described in § 72.

Each c.c. or dm. (according to whether 1 gm. or 10 gr. manure is taken for the operation) corresponds to 1 per cent. of tricalcic phosphate, rendered soluble in the process of manufacturing the manure.

4. Insoluble Phosphates containing no amount of Iron or Alumina—Mineralised Guanos, Bones, Bone Meal, Bone Ash, &c.

These may all be estimated with great exactness by simply treating a weighed quantity with hot hydrochloric acid to extract all soluble matter, well washing the insoluble residue on a filter, precipitating with ammonia, redissolving in acetic acid, and titrating the filtrate for phosphoric acid with the uranic solution just described.

The same process may be applied to the estimation of the insoluble phosphates in manures manufactured from the same phosphate as described above, first removing all the soluble matter by cold water, filtering and washing the residue well with warm water. The insoluble matter is then treated on the filter with warm hydrochloric acid to dissolve the phosphates, which can then be collected in the filtrate, precipitated with ammonia, redissolved with acetic acid, and titrated with uranium as usual.

5. Phosphates containing either Iron or Alumina or both—German Phosphorite, Staffelite, Cambridge, Suffolk, and Bedford Coprolites, Rodonda and Sombrero Guano, &c.

Methods have already been given in § 72 for the removal of P^2O^5 from these compounds, and bringing it into such a form that it may readily be estimated volumetrically. Considerable time and experience, however, are required to carry out the processes there described for manufacturers or manure works. Where no great facilities exist for general analysis, it may be desirable to give shorter methods, which, though not quite so exact, may with care and attention be made available for their purpose. It must, however, be distinctly understood that, where more than 3% or 4% of alumina exists, these methods will not apply; in such cases the P^2O^5 must be separated by the tin or bismuth processes described in § 72.

Preparation of the Raw Material for the Analysis.

Extraction of the phosphoric acid by dilute sulphuric acid. Weigh 10 gm. (or 100 grn.) of the very finely powdered phosphate in a platinum or porcelain crucible, or in a small sheet-iron pan, and place it over a gas or spirit lamp for about ten minutes, keeping it at a dull red heat; then set aside to cool; when cold transfer to a mortar, and rub it down to a fine powder, adding

gradually 200 c.c. of cold dilute sulphuric acid, containing about 5 per cent. of acid (made by mixing 50 c.c. strong acid with 950 c.c. water; if the grain system is used, 50 dm. of acid should be added to 950 dm. of water, and 200 dm. of the diluted acid used for 100 grn. phosphate).

The mixed acid and phosphate is transferred to a litre or 1000 dm. flask, as the case may be, the mortar repeatedly rinsed out first with portions of the measured acid, and lastly with water, till the measure is made up; the whole is then well shaken occasionally, and after three hours set aside to deposit, or, if necessary, at the end of three hours a portion may be filtered for the analysis.

The analytical process: This will be described entirely on the gramme system, but those who prefer to use grains can easily do so by understanding the principle explained in previous sections. Measure 100 c.c. of the clear fluid from the flask into a beaker, and add 10 drops of a saturated solution of citric acid, then neutralise with ammonia, throwing into the fluid a small piece of litmus paper and stirring well; when the paper is distinctly blue and the fluid smells of ammonia, add acetic acid until the litmus paper turns red; then add 10 c.c. of the sodic acetate solution, heat to nearly boiling, and run into the fluid the uranic solution until the testing with the prussiate gives the required colour. Each c.c. of the uranic solution required represents 1 per cent. of phosphate of lime.

Extraction of the phosphoric acid by alcohol. 1 or 2 gm. of the powdered raw phosphatic material is heated in a porcelain capsule, with sufficient hydrochloric acid to dissolve all the phosphates, and to produce a deep yellow-coloured solution containing the iron and alumina. It is allowed to cool somewhat, and some strong sulphuric acid added; this causes a thick precipitate of hydrated gypsum, but when heated the mixture becomes thinner with the separation of anhydrous gypsum. The heating is continued till vapours of sulphuric acid are given off, but not to perfect dryness; by this means all the hydrochloric acid is got rid of, and the iron and alumina both exist as basic sulphates insoluble in alcohol. The capsule is cooled, and 90 per cent. alcohol (methylated answers very well) added in tolerable quantity, then covered and set aside to digest for an hour or two, with occasional stirring. The whole is then transferred to a small filter by degrees, and the insoluble matter washed repeatedly with fresh alcohol until that which passes through no longer reddens blue litmus paper. The filtered solution contains all the phosphoric acid and some free

sulphuric acid also, but no lime, iron, or alumina. Before titrating, the alcohol must be either evaporated away to about one-third of its volume, or the filtrate may be received into a small retort connected with a condenser, and the spirit distilled off to near dryness; in either case the residue is diluted to about 100 or 200 c.c., when 1 or 2 gm. of material have been taken and neutralised with ammonia, then acidified with acetic acid, 10 c.c. sodic acetate added, and titrated with uranium as usual.

Either of these processes for the estimation of P^2O^5 in the presence of iron and alumina will give very good results when carefully performed. The method by dilute sulphuric acid has been tried upon a sample of Bedford coprolite containing about 8% iron, with some alumina. The total P^2O^5 , calculated as tricalcic phosphate, was first very carefully estimated by the molybdic method, and yielded 50.1 per cent. by weight; the same by the oxalic acid and lead process used in the Royal Agricultural College, weighed as magnesian pyrophosphate, gave 49.9%. The same, by cold dilute SO^4 and titration with uranium, gave 49.7%. The same phosphate, with the addition of 10% each of ferric oxide and dried alum before the ignition of the powdered phosphate, gave volumetrically 50.6%.

A sample of German phosphate was analysed as follows:—

1. Molybdic method, by weight,	. . .	62.24%
2. " " "	. . .	62.11%
3. Bismuth method, and titration with uranium,		61.75%
4. " " "		62.00%
5. Cold sulphuric acid, and titration with uranium,		62.00%
6. " " "		62.10%

Modification of the above Process.

Since the foregoing matter was in type, a comprehensive paper has been contributed to Fresenius' Zeitschrift (vol. x. page 133), by Drs Fresenius, Neubauer, and Luck, on the best method of analysing commercial phosphates, either in the raw or manufactured state, the end in view being to render the operation as speedy as possible, without the sacrifice of accuracy. The condensed results are as follows:—

The experiments made were mostly upon raw phosphates, containing iron and alumina—such as phosphorite from the Lahn

Valley—and upon manufactured phosphates from the same source. These are, as is well known, peculiarly liable to lose soluble phosphate by keeping, and to contain the so-called reduced phosphates.

In the raw mineral it is necessary to estimate the total Phosphoric Acid

In the Manufactured Manure.

- | | |
|--|-------|
| 1. The phosphoric acid soluble in cold water, . . . | = a |
| 2. The reduced phosphoric acid, | = b |
| 3. The insoluble phosphoric acid, | = c |
| From these data is obtained the total phosphoric acid, | |
| | = S |

Estimation of the total Phosphoric Acid in the Raw Mineral.

5 gm. of the finely-powdered phosphate is weighed, transferred to a porcelain mortar, and repeatedly rubbed with about 10 c.c. of a 5 per cent. solution of sulphuric acid, as described at page 239. 110 c.c. of the cold dilute acid to be used, the creamy mixture is transferred to a 250 c.c. flask, and the mortar repeatedly washed out with small portions of water until about 200 c.c. are contained in the flask. The mixture is shaken frequently during about four hours, then diluted to 250 c.c. exactly with water, and well mixed.

A dry filter and a dry flask are then got ready, and the liquid filtered into it, then 100 c.c. transferred to a 200 c.c. flask, rendered distinctly alkaline with caustic soda solution (to neutralise the sulphuric acid), then acetic acid added in sufficient quantity to redissolve the precipitated calcic phosphate. A cloudiness will always, however, be present if the raw substance contains iron. The whole is diluted to 200 c.c. and set aside in order that the cloudiness may deposit. This deposit will consist almost entirely of ferric phosphate, and should be filtered off through a small dry filter, the filtrate being received into a dry flask, which is corked and set aside for titration with uranium, and marked *half-strength solution*. The ferric phosphate in the filter is washed repeatedly with water (the washings being thrown away), and finally weighed as ferric phosphate.

The object of using sulphuric acid instead of nitric or hydrochloric, is that of preventing the solution of any quantity of iron or alumina. Small quantities of these, however, more especially iron, will find their way into the solution. The proportion dis-

solved seems very constant, however; and after using the process a few times, any intelligent operator will judge if any great variation occurs.

The authors here alluded to found that in the special phosphate under examination, containing 32% $P^2O^5 = 70\%$ tricalcic phosphate, the amount of P^2O^5 to allow for in the form of ferric phosphate was 2 per cent. This was in a sample containing a considerable quantity of iron. It is probable that wherever there is sufficient iron present to withdraw this quantity of P^2O^5 , this proportion of precipitate will occur whatever may be the percentage of tricalcic phosphate. The authors do not recommend that any average allowance should be made for it; but that it should be weighed. My experience, however, goes to prove that where the extraction with cold dilute sulphuric acid has been properly followed, and where it is not necessary to be absolutely accurate, the trouble of igniting and weighing the precipitate may be avoided, the error in any case being a mere fraction.

Thus far the process is very much like the one described at page 239; but a change is made in the method of titration. It is known that when a solution of phosphate, prepared as above, even with the addition of a little citric acid, is heated (after the ferric phosphate is removed), a precipitate occurs, and most operators have supposed this to be ferric phosphate. It is not so, however, but mainly calcic phosphate; and thus when such a solution is titrated with uranium, the results are too low. In order to avoid this, the process of titration is reversed, *i.e.*, instead of heating the phosphate solution and running the uranium into it, the uranium solution is heated and the phosphate run into it until no chocolate colour is produced, or only faintly, when brought in contact with a little powdered potassic ferrocyanide on a white slab.

The authors recommend a solution of uranic acetate, which should be titrated by means of a standard solution of sodic phosphate. 25 c.c. of the uranic solution is placed in a beaker, together with 5 c.c. of sodic acetate solution, and 3 c.c. acetic acid then heated in a boiling-water bath, and the sodic phosphate solution delivered in from the burette until a drop of the solution brought in contact with the prussiate just ceases to give a brown colour. Practice will soon enable an operator to understand how much phosphate solution may be run into the uranium before beginning to test, owing to the yellow colour of latter disappearing.

Having by this means established the strength of the uranium

solution, the half-strength solution of raw phosphate can now be examined as follows:—25 c.c. uranium solution is placed in a beaker in the water bath, 5 c.c. sodic acetate added, and the phosphate solution added from the burette as just described. The quantity of phosphate solution is divided by 2 to obtain the measure of original solution which corresponds to the 25 c.c. uranium.

The phosphoric acid so found, added to that contained in the ferric phosphate, will of course be the total quantity of P^2O^5 existing in the raw material.

Where 5 gm. phosphate is dissolved in only 250 c.c. acid, it is necessary to make a correction for the space occupied in the flask by the calcic sulphate produced and the insoluble matter; experience has proved this to be in the case of 70% phosphate about 0.35% P^2O^5 , consequently this must be deducted from the total found as above. Correction may be quite avoided by using a flask of 253 c.c. instead of 250 c.c.; this is, of course, easily accomplished by measuring 3 c.c. into a 250 c.c. flask, and marking the height with a diamond or file. The authors found by this modification of the uranium process the following comparative results:—

	Uranic Method, Volumetric.	Molybdic Method, by Weight.
A sample of Phosphorite = P^2O^5 ,	21.54	21.50
“ “ “ “	32.14	32.00
“ “ “ “	32.03	32.00
A Superphosphate gave soluble = P^2O^5 ,	14.45	14.29
“ “ another sample,	13.54	13.40

Examination of a Superphosphate.

1. Soluble Phosphoric Acid.

The manure is exhausted with cold water precisely as described § 81. 3, the flask, however, being well shaken for four hours, then set aside to settle, or a portion filtered for titration. This latter is to be performed precisely as just described for the raw phosphate.

2. Reduced Phosphoric Acid.

This may be estimated either directly or indirectly. The authors experimented upon the various methods proposed for this form of P^2O^5 , such as sodic bicarbonate and ammoniac oxalate, neither of which proved satisfactory, the ammoniac oxalate process they found, like myself (Chem. News), to be extremely fallacious. The pre-

ference is given by them to neutral ammoniac citrate as a means of bringing back the reduced P^2O^5 to the soluble form. The strength of the citrate solution is sp. grav. 1.090 or thereabouts. By the direct method the residue from 2 gm. of manure, after exhaustion with cold water as above, is washed out of the filter into a mortar by help of 100 c.c. nitrate solution, and rubbed to a smooth cream, then transferred to a flask and digested for half an hour at a temperature of 30° to 40° C., then filtered, washed with some water and citrate solution, and the filtrate then evaporated in a platinum capsule to dryness, ignited with sodic carbonate and potassic nitrate, then extracted with a little dilute sulphuric acid, and titrated with uranium as previously described.

This process is, however, very troublesome, and takes a long time, the indirect method is therefore to be preferred, and the operation conducted as follows :—

Two portions of the manure, weighing 2 gm. each, are respectively exhausted with cold water until the washings are no longer acid. In one of the residues the reduced, and the insoluble P^2O^5 ($b + c$) are estimated together by the uranium method—50 c.c. of 5 per cent. sulphuric acid being used to dissolve them, as in the case of the raw phosphate, by rubbing in a mortar.

The other residue of 2 gm. is rubbed with 100 c.c. ammoniac citrate solution, and digested as described for the direct process, the filtrate and washings being thrown away; the so obtained residue contained on the filter will consist only of the insoluble phosphate c ; the filter is dried, ignited, adding finally a little sodic carbonate, then dissolved with 50 c.c. dilute sulphuric acid and titrated with uranium as before.

By this means is obtained the insoluble phosphate = c which, subtracted from the previously estimated mixture of a reduced and insoluble $P^2O^5 = (b + c)$, will give the quantity of reduced $P^2O^5 = b$.

Thus is furnished the data from which may be calculated the total percentage of P^2O^5 in the manure by the equation

$$S = a + b + c \text{ is obtained } (a + b) = S - c.$$

By estimating the following proportions the complete character of the superphosphate may be gained :—

$$\begin{array}{lcl} \text{The total } P^2O^5 & = & S \\ \text{soluble } ,, & = & a \\ \text{insoluble } ,, & = & c \end{array}$$

and from these may be calculated the quantity of reduced P^2O^5 , according to the formula

$$b = S - (a + c) \quad *$$

As an example, a specimen of superphosphate of a reddish colour, showing the presence of much iron, was analysed and gave the following results:—

1. Total P^2O^5 ,	.	.	15.80% = S
2. Soluble, „	.	.	3.84% = a
3. Insoluble, „	.	.	7.12% = c

Consequently $b = 15.80 - (3.84 + 7.12) = 6.484\%$.

Appendix to § 81.

Extraction of Soluble Phosphate.

Since the foregoing article on manures was written, it appears that most of our leading analysts have agreed to adopt a different method of extracting the soluble phosphoric acid in superphosphates, &c., from that described at p. 237, which consists in first treating the material repeatedly with small quantities of cold water, and finally boiling the residue with water for some few minutes to decompose any basic phosphate which may be present, finally washing the residue with boiling water. This yields, as a rule, a larger percentage of soluble phosphate than the mere extraction by cold water, but this is of no consequence if all analysts are agreed in the method to be pursued.

ESTIMATION OF THE NORMAL AND ABNORMAL CONSTITUENTS OF NATURAL WATERS USED FOR DRINKING, BREWING, MANUFACTURING, OR GENERAL DOMESTIC PURPOSES, AND OF SEWAGE.

§ 82. The analysis of spring or river waters has for a long period received the attention of chemists, sanitary engineers, and others, but until lately no methods of examination have been produced which could be said to satisfy the demands of those who have been interested in the subject from various points of view. The researches of Clark, Frankland, Armstrong, Miller, Wanklyn, and others, have, however, now brought the whole subject into a more satisfactory form, so that it may fairly be said that, as regards accuracy of chemical processes, or interpretation of results from a sanitary point of view, very little addition is required. Considerable space will be devoted to the matter here; and as the

greater number of processes are now brought into volumetric estimations which admit of ready and accurate results, the general subject naturally falls within the scope of this work. Considerable pains have been taken to render the treatment of the matter practical and trustworthy.

Since the various processes necessitate the use of peculiar materials and apparatus, the preparation and arrangement of these will be described at some length previous to the introduction of the general subject.

THE PREPARATION OF RE-AGENTS.

A. Re-agents required for the Estimation of Ammonia.

a. Nessler's Solution.

Dissolve 62.5 gm. of potassic iodide in about 250 c.c. of distilled water, set aside a few c.c., and add gradually to the larger part a cold saturated solution of corrosive sublimate until the mercuric iodide precipitated, ceases to be redissolved on stirring. When a permanent precipitate is obtained, restore the reserved potassic iodide so as to redissolve it, and continue adding very gradually corrosive sublimate until a slight precipitate remains undissolved. (The small quantity of potassic iodide is set aside merely to avoid a large excess of corrosive sublimate.)

Next, dissolve 150 gm. of solid potassic hydrate (that usually sold in sticks or cakes) in 150 c.c. of distilled water, allow the solution to cool, add it gradually to the above solution, and make up with distilled water to one litre.

On standing, a brown precipitate is deposited, and the solution becomes clear, and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle as required.

β. Standard Solution of Ammonic Chloride.

Dissolve 1.5735 gm. of pure dry ammonic chloride in a litre of distilled water; of this take 100 c.c., and make up to a litre with distilled water. The latter solution will contain ammonic chloride corresponding to 0.00005 gm. of ammonia (NH_3) in each c.c. In use it should be measured from a narrow burette of 10 c.c. capacity divided into tenths.

γ. Sodie Carbonate.

Heat anhydrous sodie carbonate to redness in a platinum crucible for about an hour, taking care not to fuse it. Allow to cool, and whilst still warm rub it in a clean mortar so as to break any lumps which may have been formed, and transfer to a clean dry wide-mouthed stoppered bottle. Too large a quantity should not be kept in one bottle, lest by prolonged use ammoniacal impurities get in. A bottle holding about 100 c.c. is a convenient size.

δ. Water free from Ammonia.

If, when 1 c.c. of Nessler's solution (**A. a.**) is added to 100 c.c. of distilled water in a glass cylinder, standing on a white surface (*see* Estimation of Ammonia, § 83. 3), no trace of a yellow tint is visible after five minutes, the water is sufficiently pure for use. As, however, this is rarely the case, the following process must usually be adopted. Distil from a large glass retort (or better, from a copper or tin vessel holding 15–20 litres) ordinary distilled water which has been rendered distinctly alkaline by addition of sodie carbonate. A glass Liebig's condenser, or a clean tin worm should be used to condense the vapour; it should be connected to the still by a short india-rubber joint. Test the distillate from time to time with Nessler's solution, as above described, and when free from ammonia collect the remainder for use. The distillation must not be carried to dryness. Ordinary water may be used instead of distilled water, but it sometimes continues to give off traces of ammonia by the slow decomposition of organic matter.

B. Re-agents required for the Estimation of Organic Carbon and Nitrogen.

a. Water free from Ammonia and Organic Matter.

Distilled water, to which 1 gm. of potassic hydrate and 0.2 gm. of potassic permanganate per litre have been added, is boiled gently for twenty-four hours in a similar vessel to that used in preparing water free from ammonia (**A. δ.**), an inverted condenser being so arranged as to return the condensed water. At the end of that time the condenser is adjusted in the usual way, and the water carefully distilled, the distillate being tested at intervals for ammonia, as described page 258. When ammonia is no longer

found, the remainder of the distillate may be collected for use, taking care to stop short of dryness. The neck of the retort or still should point slightly upwards, so that the joint which connects it with the condenser is the highest point. Any particles carried up mechanically will then run back to the still, and not contaminate the distillate.

β. Solution of Sulphurous Acid.

Sulphurous anhydride is prepared by the action of sulphuric acid upon cuttings of metallic copper. The gas is made to bubble through water to remove mechanical impurities, and then conducted into water free from ammonia and organic matter (**B. α.**) until a saturated solution is obtained.

γ. Solution of Hydric Sodie Sulphite.

Sulphurous anhydride, prepared and washed as above, is passed into a solution of sodie carbonate made by dissolving ignited sodie carbonate (**A. γ.**) in water free from ammonia and organic matter (**B. α.**) The gas is passed until carbonic anhydride ceases to be evolved.

δ. Solution of Ferric Chloride

Is made by dissolving solid ferric chloride in distilled water. It should be moderately concentrated, and two or three drops must not contain a perceptible quantity of ammonia. It is convenient to use a bottle with a ground glass cap instead of a stopper, so that a small dropping tube may be kept in it.

ε. Cupric Oxide

Is prepared by heating to redness with free access of air, on the hearth of a reverberatory furnace, or in a muffle, copper wire cut into short pieces, or copper sheet cut into strips. That which has been made by calcining the nitrate cannot be used, as it appears to be impossible to expel the last traces of nitrogen. After use, the oxide should be extracted by breaking the combustion tube, rejecting the portion which was mixed with the substance examined. As soon as a sufficient quantity has been recovered, it must be recalcined. This is most conveniently done in an iron tube about 30 m.m. in internal diameter, and a little longer than the combustion furnace. One end should be closed with a cork, the cupric oxide poured in,

the tube placed in the combustion furnace (which is tilted at an angle of about 15° , so as to produce a current of air), the cork removed, and the tube kept at a red heat for about two hours. In a Hofmann's gas furnace, with five rows of burners, two such tubes may be heated at the same time if long clay burners are placed in the outer rows and short ones in the three inner rows. If the furnace has but three rows of burners, a rather smaller iron tube must be used. When cold, the oxide can easily be extracted, if the heat has not been excessive, by means of a stout iron wire, and should be kept in a clean dry stoppered bottle. Each parcel thus calcined should invariably be assayed by filling with it a combustion tube of the usual size, and treating it in every respect as an ordinary combustion. It should yield only a very minute bubble of gas, which should be almost wholly absorbed by potassic hydrate. The finer portions of the oxide should, after calcining, be sifted out by means of a sieve of clean copper gauze, and reserved for use as described hereafter.

ζ. Metallic Copper.

Fine copper gauze is cut into strips about 80 m.m. wide, and rolled up as tightly as possible on a copper wire so as to form a compact cylinder 80 m.m. long. This is next covered with a tight case of moderately thin sheet copper, the edges of which meet without overlapping. The length of the strip of gauze, and the consequent diameter of the cylinder, must be regulated so that it will fit somewhat loosely in the combustion tubes. A sufficient number of these cylinders being prepared, a piece of combustion tube is filled with them, and they are heated to redness in the furnace, a current of atmospheric air being passed through them for a few minutes in order to burn off organic impurity, and coat the copper gauze superficially with oxide. A current of hydrogen, dried by passing through strong sulphuric acid, is then substituted for the air, and a red heat maintained until hydrogen issues freely from the end of the tube. It is then allowed to cool, the current of hydrogen being continued, and when cold the copper cylinders are removed and kept in a stoppered bottle. After each time of using they must be heated in a stream of hydrogen as before, and are then again ready for use. The heating in air need not be repeated.

η. Solution of Potassic Bichromate

Is used as a test for and to absorb sulphurous anhydride which

may be present in the gas obtained by combustion of the water residue. It should be saturated, and does not require any special attention. The yellow neutral chromate answers equally well, but must be rendered slightly acid, lest it should absorb carbonic as well as sulphurous anhydride.

θ. Solution of Potassic Hydrate.

A cold saturated solution made by dissolving solid potassic hydrate in distilled water.

ι. Solution of Pyrogallic Acid.

A cold saturated solution, made by dissolving in distilled water solid pyrogallic acid obtained by sublimation.

κ. Solution of Cuprous Chloride.

A saturated solution of cupric chloride is rendered strongly acid with hydric chloride, a quantity of metallic copper introduced in the form of wire or turnings, and the whole allowed to stand until the solution becomes colourless.

λ. Oxygen.

Blow a bulb of about 30 c.c. capacity at the end of a piece of combustion tube, and draw out the tube so that its internal diameter for a length of about 300 m.m. is about 3 m.m. This is done in order that the capacity of the apparatus apart from the bulb may be as small as possible. Cut the tube at the wide part about 10 m.m. from the point at which the narrow tube commences, thus leaving a small funnel-shaped mouth. Then introduce, a little at a time, dried, coarsely powdered, potassic chlorate until the bulb is full. Cut off the funnel, and, at a distance of 100 m.m. from the bulb, bend the tube at an angle of 45° , and at 10 m.m. from the end bend it at right angles in the opposite direction. It then forms a retort and delivery tube in one, and must be adjusted in a mercury trough in the usual manner, taking care that the end does not dip deeper than about 20 m.m. below the surface, as otherwise the pressure of so great a column of mercury might destroy the bulb when softened by heat. On gently heating, the potassic chlorate fuses and evolves oxygen. The escaping gas is collected in test tubes about 150 m.m. long and 20 m.m. in diameter, rejecting the

first 60 or 80 c.c., which contain the nitrogen of the air originally in the bulb retort. Five or more of these tubes, according to the quantity of oxygen required, are collected and removed from the mercury trough, in very small beakers, the mercury in which should be about 10 m.m. above the end of the test tube. Oxygen may be kept in this way for any desired length of time, care being taken, if the temperature falls considerably, that there is sufficient mercury in the beaker to keep the mouth of the test tube covered. About 10 c.c. of the gas in the first tube collected is transferred by decantation in a mercury trough to another tube, and treated with potassic hydrate and pyrogallic acid, when, if after a few minutes it is absorbed with the exception of a very small bubble, the gas in that and the remaining tubes may be considered pure. If not, the first tube is rejected and the second treated in the same way, and so on.

μ. Hydric Metaphosphate.

The glacial hydric metaphosphate, usually sold in sticks, is generally free from ammonia, or very nearly so. A solution should be made containing about 100 gm. in a litre. It should be so far free from ammonia as that 10 c.c. do not contain an appreciable quantity.

ν. Tricalcic Phosphate.

Prepared by precipitating common hydric disodic phosphate with calcic chloride, washing the precipitate with water by decantation, drying, and heating to redness for an hour.

C. Re-agents required for the Estimation of Nitrogen present as Nitrites and Nitrates.

a. Solution of Argentic Sulphate.

Argentic carbonate is precipitated from the nitrate by sodic carbonate, washed well by decantation, and converted into sulphate by the addition of hydric sulphate in slight excess; the excess of acid is carefully neutralised with potassic hydrate, and the sparingly soluble argentic sulphate washed with cold water by decantation until 100 c.c. evaporated to dryness and tested as hereafter described (§ 83. 6.) are found to contain no nitrates. It should be kept in a rather large bottle filled up with distilled water, and the clear saturated solution of argentic sulphate decanted into a smaller bottle as required for use. The large bottle is replenished with water from time to time,

and well shaken on each addition until the whole of the sulphate is consumed.

β. Concentrated Hydric Sulphate.

The ordinary colourless acid is usually free from nitrates and nitrites. It should be tested before use by the method described hereafter for the estimation of nitrogen as nitrates. (§ 83. 6.)

γ. Potassic Permanganate.

Dissolve about 10 gm. crystallised potassic permanganate in a litre of distilled water.

δ. Sodie Carbonate.

Dissolve about 10 gm. of dry, or an equivalent quantity of crystallised sodie carbonate free from nitrates, in a litre of distilled water.

For the Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, but little Organic Nitrogen.

ε. Metallic Aluminium.

As thin foil.

ζ. Solution of Sodie Hydrate.

Dissolve 100 gm. of solid sodie hydrate in a litre of distilled water; when cold, put it in a tall glass cylinder, and introduce about 100 sq. c.m. of aluminium foil, which must be kept at the bottom of the solution by means of a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about one-third of its volume has been evaporated, allow to cool, and make up to its original volume with water free from ammonia. The absence of nitrates is thus ensured.

η. Broken Pumice.

Clean pumice is broken in pieces of the size of small peas, sifted free from dust, and heated to redness for about an hour.

θ. Hydric Chloride free from Ammonia.

If the ordinary pure acid is not free from ammonia, it should be rectified from sulphuric acid. As only two or three drops are used in each experiment, it will be sufficient if that quantity does not contain an appreciable proportion of ammonia.

D. Re-agents required for the Estimation of Chlorine present as Chloride.

a. Standard Solution of Argentic Nitrate.

Dissolve 2.3944 gm. of pure recrystallised argentic nitrate in distilled water, and make up to a litre. In use it is convenient to measure it from a burette which holds 10 c.c. and is divided into tenths.

β. Solution of Potassic Chromate.

A strong solution of pure neutral potassic chromate free from chlorine. It is most conveniently kept in a bottle similar to that used for the solution of ferric chloride (**B. δ.**)

E. Re-agents required for determination of Hardness.

a. Standard Solution of Calcic Chloride.

Dissolve in dilute hydric chloride, in a platinum dish, 2 gm. of pure crystallised calcite, adding the acid gradually, and having the dish covered with a glass plate, to prevent loss by spiriting. When all is dissolved, evaporate to dryness on a water bath, add a little distilled water, and again evaporate to dryness. Repeat this several times to ensure complete expulsion of hydric chloride. Lastly, dissolve the calcic chloride in distilled water, and make up to one litre.

β. Standard Solution of Potassic Soap.

Rub together in a mortar 150 parts of lead plaster (Emplast. Plumbi of the druggists) and 40 parts of dry potassic carbonate. When they are fairly mixed, add a little methylated spirit and continue triturating until a uniform creamy mixture is obtained. Allow to stand for some hours, then throw on to a filter and wash several times with methylated spirit. The strong solution of soap thus obtained must be diluted with a mixture of one volume of distilled water, and two volumes of methylated spirit (considering the soap solution as spirit), until exactly 14.25 c.c. are required to form a permanent lather with 50 c.c. of the standard calcic chloride (**E. a.**), the experiment being performed precisely as in determining the hardness of a water. A preliminary assay should be made with a small quantity of the strong soap solution to ascertain its strength.

It is better to make the solution a little too strong at first, and dilute it to the exact strength required, as it is easier to add alcohol accurately than strong soap. After making the solution approximately of the right strength, allow it to stand twenty-four hours; and then, if necessary, filter it, and afterwards adjust its strength accurately.

THE ANALYSIS OF NATURAL WATERS AND SEWAGE.

§ 83. The purest form of natural water is rain, the only impurities in which are traces of organic matter, ammonia, and ammoniac nitrate derived from the atmosphere. On reaching the ground it becomes more or less charged with the soluble constituents of the soil, such as calcic and magnesian carbonates, potassic and sodic chlorides and other salts, which are dissolved, some by a simple solvent action, others by the agency of carbonic acid in solution. Draining off from the land, it will speedily find its way to a stream which, in the earlier part of its course, will probably be free from pollution by animal matter, except that derived from any manure which may have been applied to the land on which the rain fell. Thus comparatively pure, it will furnish a supply of water to the inhabitants on its banks, which after use will be returned to the stream in the form of sewage charged with impurity derived from animal excreta, soap, household refuse, &c., the pollution being perhaps lessened by submitting the sewage to some purifying process such as irrigation of land, filtration, or clarification. The stream in its subsequent course to the sea will be in some measure purified by slow oxidation of the organic matter and by the absorbent action of vegetation, but not to any great extent. Some of the rain will not, however, go directly to a stream, but sink through the soil to a well. If this be shallow, it may be considered as merely a pit for the accumulation of drainage, and being in most cases close to a dwelling, the soil will be almost inevitably charged with excretal and other refuse, so that the water when it reaches the well will be contaminated with soluble impurities thence derived, and with nitrites and nitrates resulting from their oxidation. After use the water from the well will, like the river water, form sewage, and find its way to a river, or again to the soil, according to circumstances.

In the case of a deep well from which the surface water is excluded, the conditions are different. The shaft will usually pass through an impervious stratum, so that the water entering it will not be derived from the rain which falls on the area immediately surround-

ing its mouth, but from that which falls on the outcrop of the pervious stratum below the impervious one just mentioned ; and if this be uninhabited, the water of the well will probably be entirely free from organic impurity or products of decomposition ; but even if the water be polluted at its source, still it must pass through a very extensive filter before it reaches the well, and its organic matter will probably be in great measure converted by oxidation into bodies in themselves innocuous.

This is very briefly the general history of natural waters, and the problem presented to the analyst is to ascertain the quality and quantity of the impurities present, and, as far as possible, the previous history of the water.

To form for sanitary purposes an opinion of the character of a natural water or sewage, it will in most cases suffice to determine the ammonia, organic carbon, organic nitrogen, total solid matter, nitrogen as nitrates and nitrites, suspended matter, chlorine, and hardness, and in the following pages the estimation of these will be considered in detail, and then more briefly that of other impurities.

The method of estimating ammonia is substantially that described by the late Dr W. A. Miller in the *Journal of the Chemical Society*, ser. ii., vol. 3, p. 125 ; and those for estimating organic carbon and nitrogen, and nitrogen as nitrates and nitrites, were devised by Drs Frankland and Armstrong, and described by them in the same journal, ser. ii., vol. 6, p. 77 *et seq.*

1. Collection of Samples.

The points to be considered under this head are the vessel to be used, the quantity of water required, and the method of ensuring a truly representative sample.

Stoneware bottles should be avoided, as they are apt to affect the hardness of the water, and are more difficult to clean than glass. Stoppered glass bottles should be used if possible ; the kind known as "Winchester quarts," which hold about two and a half litres each, are very convenient and easy to procure. One of these will contain sufficient for the general analysis of sewage and largely polluted rivers, two for well waters and ordinary rivers and streams, and three for lakes and mountain springs. If a more detailed analysis is required, of course a larger quantity must be taken.

If corks are used, they should be *new*, and well washed with the water at the time of collection.

In collecting from a well, river, or tank, plunge the bottle itself,

if possible, below the surface ; but if an intermediate vessel must be used, see that it is thoroughly clean and well rinsed with the water. Avoid the surface water and also any deposit at the bottom.

If the sample is taken from a pump or tap, take care to let the water which has been standing in the pump or pipe run off before collecting, then allow it to flow directly into the bottle. If it is to represent a town water supply, take it from the service pipe, and not from a cistern.

In every case, first fill the bottle completely with the water, empty it again, rinse once or twice carefully with the water, and then fill it nearly to the stopper, and tie down tightly.

2. Preliminary Observations.

In order to ensure uniformity, the bottle should invariably be well shaken before taking out a portion of the sample for any purpose. The *colour* should be observed as seen in a tall, narrow cylinder standing upon a white surface. It is well to compare it with distilled water in a similar vessel. The *taste* and *odour* are most easily detected when the water is heated to 30°–35° C.

Before commencing the quantitative analysis, it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. As a general rule, if the suspended matter is to be determined, the water should be filtered before the estimation of organic carbon and nitrogen, ammonia, and total solid residue ; if otherwise, it should merely be shaken up. If the suspended matter is *not* determined, the appearance of the water, as whether it is clear or turbid, should be noted.

3. Estimation of Ammonia.

Place about 50 c.c. of the water in a glass cylinder about 150 m.m. high, and of about 50 c.c. capacity, standing upon a white glazed tile or white paper. Add about 1 c.c. of Nessler's solution (**A. a.**), stir with a clean glass rod, and allow to stand for a minute or so. If the colour then seen does not exceed in intensity that produced when 0.1 c.c. of the standard ammoniac chloride (**A. β.**) is added to 50 c.c. of water free from ammonia (**A. δ.**), and treated in the same way, half a litre of the water should be used for the estimation. If it does, a proportionately smaller quantity should be taken, but it is not convenient to use less than 20 or 25 c.c.

If it has been decided that the water should be filtered before

analysis, care must be taken, should it contain only a small quantity of ammonia, that the *filter paper* is free from ammonia. If it is not, it must be steeped in water free from ammonia for a day or so, and when used, the first portion of the filtrate rejected. *Washing* with water, even if many times repeated, is generally ineffectual. When a large quantity of ammonia is present, as in highly polluted water and sewage, any ammonia in the filter paper may be neglected. A moderate quantity of suspended matter may also generally be neglected with safety, even if the water is to be filtered in estimating organic carbon and nitrogen and total solid matter.

The water, filtered or unfiltered as the case may be, should be carefully measured and introduced into a capacious retort, connected by an india-rubber joint with a Liebig's condenser, the volume being, if necessary, made up to about 400 c.c. with water free from ammonia. Add about 1 gm. of sodic carbonate (A. γ.), and distil rapidly, applying the lamp flame directly to the retort, and collect the distillate in a small glass cylinder, such as is described above. When the first cylinder is full, put it aside and collect a second, and as soon as that is full remove the lamp, and add to the *second* distillate about 1 c.c. of Nessler's solution, stir with a clean glass rod, and allow to stand on a white tile or sheet of paper for five minutes. To estimate the ammonia present, measure into a similar cylinder as much of the standard ammoniac chloride solution as you judge by the colour to be present in the distillate, make it up with water free from ammonia to the same volume, and treat precisely in the same way with Nessler's solution. If on standing the intensity of colour in the two cylinders is equal, the quantity of ammonia is also equal, and this is *known* in the trial cylinder. If it is not equal, another trial must be made with a greater or less quantity of ammoniac chloride. The ammoniac chloride must not be added *after* the Nessler's solution, or a turbidity will be produced which entirely prevents accurate comparison. If the ammonia in the second distillate does not exceed that in 0.2 c.c. of the standard ammoniac chloride, the distillation need not be proceeded with any farther, but if otherwise, successive quantities must be distilled and tested until ammonia ceases to be found. If the ammonia in the second distillate corresponds to 0.4 c.c. or less of the ammoniac chloride, that in the first may be estimated in the same way, but if the second contains more ammonia than that, the first must be measured and an aliquot part taken and diluted to about 50 c.c. with water free

from ammonia, as it is likely to contain so much ammonia as to give a colour too intense to admit of easy comparison. A colour produced by more than 2 c.c. of ammoniac chloride cannot be conveniently employed. When, as in the case of sewage, a large quantity of ammonia is known to be present, it saves trouble to distil about 100 c.c. first, and at once take an aliquot part of that as above described. If the liquid spirits in distilling, arrange the retort so that the joint between the retort and condenser is the highest point; the distillation will proceed rather more slowly, but anything carried up mechanically will be returned to the retort. When the ammonia has been estimated in all the distillates, add together the corresponding volumes of ammoniac chloride solution; then, if 500 c.c. have been distilled, this in cubic centimetres divided by 100 will give the quantity of ammonia (NH^3) in 100,000 pts. of the water; if less than that, say y c.c. have been used, multiply the volume of ammoniac chloride by $\frac{500}{y}$ and divide by 100 as before.

4. Estimation of Organic Carbon and Nitrogen.

This should be commenced as soon as the ammonia has been determined. If the ammonia is less than 0.1 part per 100,000, a litre should be used; if more than 0.1, and less than 0.5, half a litre; if more than 0.5, and less than 1.0, a quarter of a litre; if more than 1.0, a hundred c.c. or less. These quantities are given as a guide in dealing with ordinary waters and sewage, but subject to variation in exceptional cases. A quantity which is too large should be avoided as entailing needless trouble in evaporation, and an inconveniently bulky residue and resulting gas. If it is to be filtered before analysis, the same precaution as to filter paper must be taken as for estimation of ammonia.

Having measured the quantity to be used, add to it in a capacious flask 15 c.c. of the solution of sulphurous acid (**B. β .**), and boil briskly for a few seconds, in order to decompose the carbonates present. Evaporate to dryness in a hemispherical glass dish, about a decimetre in diameter, and preferably without a lip, placed over a steam or water bath, as much of its surface as possible being exposed to the action of the steam. Add to the first dishful two or three drops of the solution of ferric chloride (**B. δ .**); and, if the water contained little or no carbonate, one or two c.c. of hydric sodic sulphite (**B. γ .**) The former greatly facilitates the destruction of the nitrites and nitrates by the sulphurous acid, and the latter combines with the sulphuric acid formed by the oxidation of the

sulphurous acid, which would, if free, decompose the organic matter when concentrated by evaporation. An idea of the quantity of carbonate present, sufficiently accurate for this purpose, may generally be formed from the quantity of precipitate thrown down, on addition of sodic carbonate in the ammonia estimation.

During the whole of the evaporation the dish must be kept covered with a drum or disc of filter paper made by stretching the paper by means of two hoops of light split cane, one thrust into the other, the paper being between them, in the way often employed in making dialysers. This protects the water from dust, and also, to a great extent, from ammonia which may be in the atmosphere, and which would impair the accuracy of the results. As the glass dish would be in some danger of breaking by the introduction of *cold* water, the flask containing the water being evaporated must be kept on a hot plate or sand bath at a temperature of about 60° or 70° C., and should be covered with a watch glass. If, at any time, the water in the dish or flask ceases to smell strongly of sulphurous acid, more should be added. The preliminary boiling may be omitted when less than 250 c.c. is used. When the nitrogen as nitrates and nitrites exceeds 0.5 part, the dish, after the evaporation has been carried to dryness, should be filled with distilled water containing ten per cent. of saturated sulphurous acid solution, and the evaporation again carried to dryness; if it exceeds 1.0 part, a quarter of a litre of this solution should be evaporated on the residue; 2.0 parts, half a litre; and if 5 parts, a litre. The estimation of nitrogen as nitrates and nitrites will usually be accomplished before this stage of the evaporation is reached.

In the case of sewage, however, it is advisable to employ hydric metaphosphate in the place of sulphurous acid, as the ammonic phosphate is even less volatile than the sulphite. This can only be employed for sewage and similar liquids, which are free from nitrates and nitrites. To the measured quantity of liquid to be evaporated, add, in the glass dish, 10 c.c. of the hydric metaphosphate (**B. μ .**), and, in order to render the residue more convenient to detach from the dish, about half a gramme of tricalcic phosphate (**B. ν .**), and proceed as usual. No ferric chloride, sulphurous acid, or sodic sulphite is required; nor is it necessary to boil before commencing the evaporation.

The next operation is the combustion of the residue. The combustion tube should be of hard, difficultly fusible glass, with an internal diameter of about 10 m.m. Cut it in lengths of about

430 m.m., and heat one end of each in the blowpipe flame to round the edges. Wash it well with water, brushing the interior carefully with a tube brush introduced at the end whose edges have been rounded, rinse with distilled water, and dry in an oven. When dry, draw off and close, at the blowpipe, the end whose edge has been left sharp. The tube is then ready for use.

Pour on to the perfectly dry residue in the glass dish, standing on a sheet of white glazed paper, a little of the fine cupric oxide (**B. ε.**), and with the aid of a small elastic steel spatula (about 100 m.m. long and 15 m.m. wide) carefully detach the residue from the glass and rub it down with the cupric oxide. The spatula readily accommodates itself to the curvature of the dish and effectually scrapes its surface. When the contents of the dish are fairly mixed, fill about 30 m.m. of the length of the combustion tube with granulated cupric oxide (**B. ε.**), and transfer the mixture in the dish to the tube. This is done in the usual way by a scooping motion of the end of the tube in the dish, the last portions being transferred by the help of a bent card. Rinse the dish twice with a little fine cupric oxide, rubbing it well round each time with the spatula, and transfer to the tube as before. Any particles scattered on the paper are also to be put in. Fill up to a distance of 270 m.m. from the closed end with granular cupric oxide, put in a cylinder of metallic copper (**B. ζ.**), and then again 20 m.m. of granular cupric oxide. This last is to oxidise any traces of carbonic oxide which might be formed from carbonic anhydride by the reducing action of iron present as an impurity in the metallic copper. Now draw out the end of the tube so as to form a neck about 100 m.m. long and 4 m.m. in diameter, fuse the end of this to avoid injury to the india-rubber connector, and bend it at right angles. It is now ready to be placed in the combustion furnace and attached to the Sprengel pump.

The most convenient form of this instrument for the purpose is shown in fig. 28. The glass funnel *a* is kept supplied with mercury, and is connected by a caoutchouc joint with a long narrow glass tube which passes down nearly to the bottom of a wider tube *d*, 900 m.m. long, and 10 m.m. in internal diameter. The upper end of *d* is cemented into the throat of a glass funnel *c* from which the neck has been removed. A screw clamp *b* regulates the flow of mercury down the narrow tube. A piece of ordinary glass tube *f g*, about 6 m.m. in diameter and 600 m.m. in length, is attached at *g* to a tube *gh k*, about 6 m.m. in diameter, 1500 m.m. long, with a bore of 1 m.m. This is bent sharply on itself at *h*, the part *h k*

being 1300 m.m. long, and the two limbs are firmly lashed together with copper wire at two points, the tubes being preserved from injury by short sheaths of caoutchouc tube. The end *k* is recurved

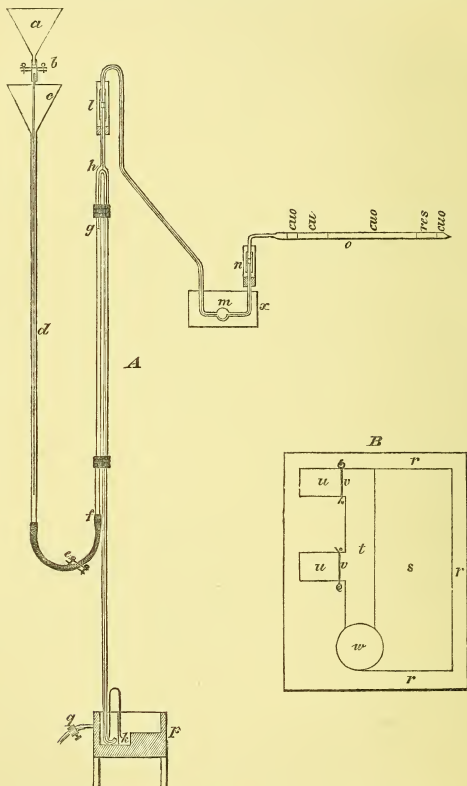


Fig. 28.

for the delivery of gas. At the top of the bend at *h*, a piece of tube *h l*, about 120 m.m. long, and 5 m.m. in diameter, is sealed on. The whole *l k* is kept in a vertical position by a loose support or guide, near its upper part, the whole of its weight resting on the

end *k*, so that it is comparatively free to move. It is connected at *f* with the lower end of *d*, by means of a piece of caoutchouc tube covered with tape, and furnished with a screw clamp *e*. At *l* it is connected with the combustion tube *o*, by the connecting tube *l m n*, which is made of tube similar to that used for *h k*. A cork slides on *h l*, which is fitted into the lower end of a short piece of tube of a width sufficient to pass easily over the caoutchouc joint connecting the tubes at *l*. After the joint has been arranged (the ends of the tubes just touching) and bound with wire, the cork and wide tube are pushed over it and filled with glycerine. The joint at *n* is of exactly the same kind, but as it has to be frequently disconnected, water is used instead of glycerine, and the caoutchouc is not bound on to the combustion tube with wire. It will be seen that the joint at *l* is introduced chiefly to give flexibility to the apparatus. At *m* is a small bulb blown on the tube for the purpose of receiving water produced in the combustion. This is immersed in a small water trough *x*. The tube *h k* stands in a mercury trough *p*, which is shown in plan on a larger scale at B.

This trough should be cut out of a solid piece of mahogany, as it is extremely difficult to make joints to resist the pressure of such a depth of mercury. It is 200 m.m. long, 155 m.m. wide, and 100 m.m. deep, outside measurement. The edge *r r* is 13 m.m. wide, and the shelf *s* 65 m.m. wide, 174 m.m. long, and 50 m.m. deep from the top of the trough. The channel *t* is 25 m.m. wide, and 75 m.m. deep, having at one end a circular well *w*, 42 m.m. in diameter, and 90 m.m. deep. The recesses *u u* are to receive the ends of two Sprengel pumps. They are each 40 m.m. long, 25 m.m. wide, and of the same depth as the channel *t*. A short iron wire *v* stretches across each of these, and serves to support the test tubes, in which the gas delivered by the pump is collected. The trough stands upon four legs 75 m.m. high, and is provided at the side with a tube and screw clamp *q*, by which the mercury may be drawn off to the level of the shelf *s*.

The combustion tube being placed in the furnace, protected from the direct action of the flame by a sheet-iron trough lined with asbestos, and the water joint at *n* adjusted, the front part of the furnace is lighted so as to heat the whole of the metallic copper and part of the cupric oxide.

At the same time a stream of mercury is allowed to flow from the funnel *a*, which fills the tubes *d* and *f* until it reaches *h*, when it falls in a series of pellets down the narrow tube *h k*, each carrying

before it a quantity of air drawn from the combustion tube. The flow of mercury must be controlled by means of the clamps *b* and *e*, so as not to be too rapid to admit of the formation of these separate pistons, and especially, care should be taken not to permit it to go so fast as to mount into the connecting tube *l m n*, as it cannot be removed thence except by disconnecting the tube. During the exhaustion, the trough *x* is filled with hot water in order to expel any water condensed from a previous operation. In about ten minutes the mercury will fall in the tube *h k* with a loud sharp clicking sound, showing that the vacuum is complete. As soon as this occurs, the pump may be stopped, a test tube filled with mercury inverted over the delivery end of the tube *k*, cold water substituted for hot in the trough *x*, and the combustion proceeded with in the usual way. This will take from fifty to sixty minutes. As soon as the whole of the tube is heated to redness, the pump is again worked, and the gases produced transferred to the tube placed to receive them. When the combustion tube is completely exhausted, the test tube of gas may be removed in a small beaker, and transferred to the gas analysis apparatus.

This gas collected consists of carbonic anhydride, nitric oxide, and nitrogen, and (rarely) carbonic oxide, which can readily be separated and estimated by the ordinary methods of gas analysis. This is rapidly accomplished with the apparatus described in part vii. § 91, or the simpler form, shown in the accompanying diagram, which, whilst it does not permit of analysis by explosion, leaves nothing to be desired for this particular operation. It is essentially that described by Frankland in the Journal of the Chemical Society, ser. ii. vol. vi. p. 109, but is slightly modified in arrangement. In the diagram, *a c d* is a measuring tube, of which the cylindrical portion *a* is 370 m.m. long, and 18 m.m. in internal diameter, the part *c* 40 m.m. long, and 7 m.m. in diameter, and the part *d* 175 m.m. long, and 2.5 m.m. in diameter. To the upper end of *d* a tube, with a capillary bore and stopcock *f*, is attached, and bent at right angles. Allowing 20 m.m. for each of the conical portions at the joints between *a* and *c*, and *c* and *d*, and 25 m.m. for the vertical part of the capillary tube, the vertical measurement of the entire tube is 650 m.m. It is graduated carefully, from below upward, at intervals of 10 m.m., the zero being about 100 m.m. from the end, as about that length of it is hidden by its support, and therefore unavailable. The topmost 10 m.m. of *d*, should be divided into single millimetres. At the free end of the capillary tube a small

steel cap, shown in fig. 30, B, is cemented gas tight. The lower end of *a* is drawn out to a diameter of 5 m.m. The tube *b* is about 1·2 metre long, and 6 m.m. internal diameter, is drawn out like *a* at

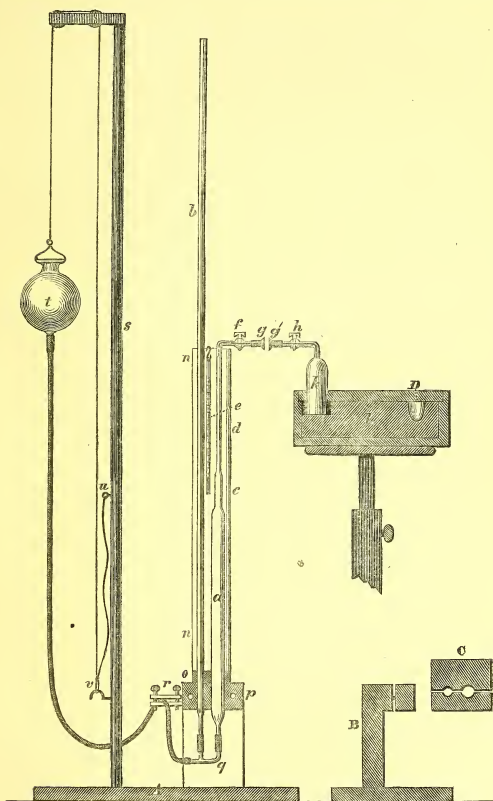


Fig. 29.

the lower end, and graduated in millimetres from below upward, the zero being about 100 m.m. from the end. The tubes *a c d* and *b* pass through a caoutchouc stopper *o*, which fits into the lower end

of a glass cylinder $n n$, intended to contain water to give a definite temperature to the gas in measuring. The zeros of the graduations should be about 10 m.m. above this stopper. Immediately below this the tubes are firmly clasped by the wooden clamp p (shown in end elevation and plan at fig. 29, B, C), the two parts of which are drawn together by two screws, the tubes being protected from breakage by a piece of caoutchouc tube fitted over each. The clamp is supported on an upright piece of wood, screwed firmly to the base A. If the stopper o is carefully fitted, and the tubes tightly clamped, no other support than p will be necessary. The tubes below the clamp are connected by joints of caoutchouc covered with tape, and strongly bound with wire, to the vertical legs of the union piece q , to the horizontal leg of which is attached a long caoutchouc tube of about 2 m.m. internal diameter, which passes to the glass reservoir t . This tube must be covered with strong tape, or have a lining of canvas between two layers of caoutchouc, as it will be exposed to considerable pressure. In its course it passes through the double screw steel pinch-cock r , the lower bar of which is fixed to the side of the clamp p .

In the base A is fixed a stout iron rod, 1.4 metre long, with a short horizontal arm at its upper end containing two grooved pulleys. The reservoir t is suspended by a cord passing over these pulleys, and attached to an eye u in the iron rod, the length of the cord being such that, when at full stretch, the bottom of the reservoir is level with the bottom of the clamp p . A loop is made on the cord, which can be secured by a hook v on the rod, so that, when thus



Fig. 30.

suspended, the bottom of t is about 100 m.m. above the stopcock f . A thermometer e , suspended by a wire hook from the edge of the cylinder $n n$, gives the temperature of the contained water, the uniformity of which may be insured by passing a slow succession of bubbles of air through it, or by moving up and down in it a wire with its end bent into the form of a ring. The jar k is called the laboratory vessel, and is 100 m.m. high, and 38 m.m. in internal diameter,

having a capillary tube, glass stopcock, and steel cap $g\ h$ exactly like $f\ g$. The mercury trough l is shown in figs. 31 and 32. It is of solid mahogany, 265 m.m. long, 80 m.m. broad, and 90 m.m. deep, outside measurement. The rim $a\ a\ a\ a$ is 8 m.m. broad, and 15 m.m. deep. The excavation b is 230 m.m. long, 26 m.m. broad, and 65 m.m. deep, with a circular cavity to receive the laboratory vessel sunk at one end, 45 m.m. in diameter, and 20 m.m. in depth below the top of the excavation. Two small lateral indentations $c\ c$, fig. 32, near the other end accommodate a capsule for transferring to the trough, tubes containing gas. This trough rests upon a telescope table, which can be fixed at any height by means of a screw, and is supported on three feet. It must be arranged, so that when the laboratory vessel is in its place in the trough, the two steel caps exactly correspond.

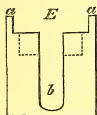


Fig. 31.

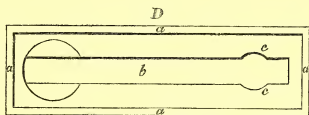


Fig. 32.

The difference of level of the mercury in the tubes b and $a\ c\ d$, caused by capillary action, when both are freely open to the air, must be ascertained by taking several careful observations. This will be different for each of the portions $a\ c$ and d , and must be added to or deducted from the observed pressure, as the mercury when thus freely exposed in both tubes to the atmospheric pressure stands in $a\ c$ or d above or below that in b . This correction will include any necessary for difference of level of the zeros of the graduations of the two tubes, and, if the relative positions of these be altered, it must be redetermined. A small telescope, sliding on a vertical rod, should be used in these and all other readings of the level of mercury.

The capacity of the measuring tube $a\ c\ d$ at each graduation must now be determined. This is readily done by first filling the whole apparatus with mercury, so that it drips from the cap g . The stopcock f is then closed, a piece of caoutchouc tube slipped over the cap, and attached to a funnel supplied with distilled water. The reservoir t being lowered, the clamp r and the stopcock f are opened, so that the mercury returns to the reservoir drawing water through the capillary tube. As soon as it is below the zero of the

graduation, the stopcock *f* is closed, the funnel and caoutchouc tube removed from the cap, and the face of the last slightly greased in order that water may pass over it without adhering. Now raise the reservoir, open the stopcock *f*, and allow the water to flow gently out until the top of the convex surface of the mercury in *a* just coincides with the zero of the graduation. The mercury should be controlled by the clamp *r*, so that the water issues under very slight pressure. Note the temperature of the water in the water jacket, and proceed with the expulsion of the water, collecting it as it drops from the steel cap in a small carefully weighed glass flask. When the mercury has risen through 100 m.m. stop the flow of water, and weigh the flask. The weight of water which was contained between the graduations 0 and 100 on the tube is then known, and if the temperature be 4° C., the weight in grammes will express the capacity of that part of the tube in cubic centimetres. If the temperature be other than 4° C., the volume must be calculated by the aid of the co-efficient of expansion of water by heat. In a similar way the capacity of the tube at successive graduations about 100 m.m. apart is ascertained, the last determination in *a* being at the highest, and the first in *c* at the lowest graduation on the cylindrical part of each tube; the tube between these points and similar points on *c* and *d* being so distorted by the glass blower that observations could not well be made. The capacity at a sufficient number of points being ascertained, that at each of the intermediate graduations may be calculated, and a table arranged with the capacity marked against each graduation. As the calculations in the analysis are made by the aid of logarithms, it is convenient to enter on this table the logarithms of the capacities instead of the natural numbers.

In using the apparatus, the stopcocks on the measuring tube and laboratory vessel should be slightly greased with a mixture of resin cerate and oil, the whole apparatus carefully filled with mercury, and the stopcock *f* closed; next place the laboratory vessel in its place in the mercury trough, and suck out the air. This is readily and rapidly done by the aid of a short piece of caoutchouc tube, placed in the vessel just before it is put into the mercury trough, and drawn away as soon as the air is removed. Suck out any small bubbles of air still left through the capillary tube, and as soon as the vessel is entirely free from air close the stopcock. Slightly grease the faces of both caps with resin cerate (to which a little oil should be added if very stiff), and clamp them tightly together. On opening both stopcocks mercury should flow freely through the

capillary communication thus formed, and the whole should be quite free from air. To ascertain if the joints are all in good order, close the stopcock *h*, and lower the reservoir *t* to its lowest position; the joints and stopcocks will thus be subjected to a pressure of nearly half an atmosphere, and any leakage would speedily be detected. If all be right, restore the reservoir to its upper position.

Transfer the tube containing the gas to be analysed to an ordinary porcelain mercury trough, exchange the beaker in which it has been standing for a small porcelain capsule, and transfer it to the mercury trough *l*, the capsule finding ample room where the trough is widened by the recess *D*.

Carefully decant the gas to the laboratory vessel, and add a drop or two of potassic bichromate solution (**B. η .**) from a small pipette with a bent capillary delivery tube, to ascertain if the gas contains any sulphurous anhydride. If so, the yellow solution will immediately become green from the formation of a chromic salt, and the gas must be allowed to stand over the chromate for four or five minutes, a little more of the solution being added if necessary. The absorption may be greatly accelerated by gently shaking from time to time the stand on which the mercury trough rests, so as to cause the solution to wet the sides of the vessel. With care this may be done without danger to the apparatus. Mercury should be allowed to pass slowly into the laboratory vessel during the whole time, as the drops falling tend to maintain a circulation in the gas. The absence of sulphurous anhydride being ascertained, both stopcocks are set fully open, the reservoir *t* lowered, and the gas transferred to the measuring tube. The stopcock *h* should be closed as soon as the liquid from the laboratory vessel is within about 10 m.m. of it. The bore of the capillary tube is so fine that the gas contained in it is too little to affect the result. Next bring the top of the meniscus of mercury seen through the telescope exactly to coincide with one of the graduations on the measuring tube, the passage of mercury to or from the reservoir being readily controlled by the pinchcock *r*. Note the position of the mercury in the measuring tube and in the pressure tube *b*, the temperature of the water-jacket, and the height of the barometer, the level of the mercury in the tubes and barometer being read to a tenth of a m.m. and the thermometer to 0.1° C. This done, introduce into the laboratory vessel from a pipette with a bent point a few drops of potassic hydrate solution (**B. θ .**), and return the gas to the laboratory vessel. The absorption of carbonic anhydride will be complete in about

three to five minutes, and if the volume of the gas is large, may be much accelerated by gently shaking the stand from time to time, so as to throw up the liquid on the sides of the vessel. If the small pipettes used to introduce the various solutions be removed from the mercury trough gently, they will always contain a little mercury in the bend, which will suffice to keep the solution from flowing out, and they may be kept in readiness for use standing upright in glass cylinders or other convenient supports. At the end of five minutes the gas, which now consists of nitrogen and nitric oxide, is again transferred to the measuring tube, and the operation of measuring repeated; the barometer, however, need not be observed, under ordinary circumstances, more than once for each analysis, as the atmospheric pressure will not materially vary during the twenty-five to thirty minutes required. Next pass into the laboratory vessel a few drops of saturated solution of pyrogalllic acid (**B. ι.**), and return the gas upon it. The object of adding the pyrogalllic acid at this stage is to ascertain if oxygen is present, as sometimes happens when the total quantity of gas is very small, and the vacuum during the combustion but slightly impaired. Under such circumstances, traces of oxygen are given off by the cupric oxide, and pass so rapidly over the metallic copper as to escape absorption. This necessarily involves the loss of any nitric oxide which also escapes the copper, but this is such a very small proportion of an already small quantity that it will not greatly affect the result. If oxygen be present, allow the gas to remain exposed to the action of the pyrogallate, until the liquid when thrown up the sides of the laboratory vessel runs off without leaving a dark red stain. If oxygen be not present, a few bubbles of that gas (**B. λ.**) are introduced to oxidise the nitric oxide to pernitric oxide, which is absorbed by the potassic hydrate. The oxygen may be very conveniently added from the gas pipette shown in fig. 33,

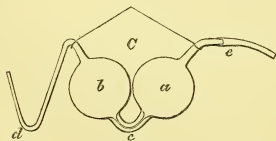


Fig. 33.

where *a b* are glass bulbs of about 50 m.m. diameter, connected by a glass tube, the bore of which is constricted at *c*, so as to allow mercury to pass but slowly from one bulb to the other, and thus control the passage of gas through the

narrow delivery tube *d*. The other end *e* is provided with a short

piece of caoutchouc tube, by blowing through which any desired quantity of gas may be readily delivered. Care must be taken after use that the delivery tube is not removed from the trough until the angle *d* is filled with mercury.

To replenish the pipette with oxygen, fill the bulb *b* and the tubes *c* and *d* with mercury, introduce the point of *d* into a tube of oxygen standing in the mercury trough, and draw air from the tube *e*. The gas in *b* is confined between the mercury in *c* and that in *d*.

When the excess of oxygen has been absorbed as above described, the residual gas, which consists of nitrogen, is measured, and the analysis is complete.*

There are thus obtained three sets of observations, from which by the usual methods we may calculate A the total volume, B the volume of nitric oxide and nitrogen, and C the volume of nitrogen, all reduced to 0° C. and 760 m.m. pressure; from these may be obtained

$$\begin{aligned} A - B &= \text{vol. of CO}^2 \\ \frac{B - C}{2} + C &= \frac{B + C}{2} = \text{vol. of N,} \end{aligned}$$

and hence the weight of carbon and nitrogen can be readily found.

It is much less trouble, however, to assume that the gas in all three stages consists wholly of nitrogen; then, if A be the weight of the total gas, B its weight after treatment with potassic hydrate, and C after treatment with pyrogallate, the weight of carbon will be $(A - B) \frac{3}{7}$ and weight of nitrogen $\frac{B + C}{2}$, for the weights of carbon and nitrogen in equal volumes of carbonic anhydride and nitrogen, at the same temperature and pressure, are as 6 : 14; and the weights of nitrogen in equal volumes of nitrogen and nitric oxide are as 2 : 1.

The weight of 1 c.c. of nitrogen at 0° C. and 760 m.m. is 0.0012562 gm., and the formula for the calculation is $w = \frac{0.0012562 \times v \times p}{(1 + 0.00367 t) 760}$,

* When the quantity of carbon is very large indeed, traces of carbonic oxide are occasionally present in the gas, and will remain with the nitrogen after treatment with alkaline pyrogallate. When such excessive quantities of carbon are found, the stopcock *f* should be closed when the last measurement is made, the laboratory vessel detached, washed, and replaced filled with mercury. Introduce then a little solution of cuprous chloride (B. z.), and return the gas upon it. Any carbonic oxide will be absorbed, and after about five minutes the remaining nitrogen may be measured.

in which w = the weight of nitrogen, v the volume, p the pressure corrected for tension of aqueous vapour, and t the temperature in degrees centigrade. To facilitate this calculation, there is given in

Table 3 the logarithmic value of the expression $\frac{0.0012562}{(1 + 0.00367 t)^{760}}$ for each tenth of a degree from 0° to 29.9° C, and in Table 4 the tension of aqueous vapour in millimetres of mercury. As the measuring tube is always kept moist with water, the gas when measured is always saturated with vapour.

The following example will show the precise mode of calculation:—

	A	B	C
	Total.	After absorption of CO_2 .	Nitrogen.
Volume of gas,	4.4888 c.c.	0.26227 c.c.	0.26227 c.c.
Temperature,	13.5 ⁰ m.m.	13.6 ⁰	13.7 ⁰
Height of mercury in a, c, d ,	315.2	485.3	485.3
„ „ „ b ,	198.7	348.8	333.5
Difference,	116.5	136.5	151.8
Plus tension of aqueous vapour at 13.5° C, . . .	11.5	11.6	11.7
	128.0		
Deduct correction for capil- larity,	0.9	Add for } 2.2 capillarity }	2.2
	127.1	150.3	165.7
Deduct this from height . .	769.8	769.8	769.8
of barometer,	127.1	150.3	165.7
Pressure on dry gas, . . .	642.7	619.5	604.1
Log. of volume of gas, . . .	0.65213	1.41875	1.41875
„ $\frac{0.0012562}{(1 + 0.00367 t)^{760}}$	6.19724	6.19709	6.19694
„ pressure on dry gas,	2.80801	2.79204	2.78111
	3.65738	4.40788	4.39680
Log. of weight of gas calcu- lated as N, =	0.0045434	0.0002558	0.0002494 gm.

From these weights, those of carbon and of nitrogen are obtained by the use of the formulæ above mentioned. Thus—

$$\begin{array}{rcl}
 A - B & = & 0.0042876 \\
 \times & & 3 \\
 \div 7 &) & 0.0128628 \\
 \text{Weight of carbon,} & & \underline{0.001837}
 \end{array}
 \qquad
 \begin{array}{rcl}
 B + C & = & 0.0005052 \\
 \div 2 & & \\
 \text{Weight of nitrogen,} & & \underline{0.0002526}
 \end{array}$$

When carbonic oxide is found, the corresponding weight of nitrogen may be found in a similar manner, and should be added

to that corresponding to the carbonic anhydride before multiplying by $\frac{3}{7}$, and must be deducted from the weight corresponding to the volume after absorption of carbonic anhydride.

As it is impossible to attain to absolute perfection of manipulation and materials, each analyst should make several blank experiments by evaporating a litre of pure distilled water (**B. a.**) with the usual quantities of sulphurous acid and ferric chloride, and, in addition, 0.1 gm. of freshly ignited sodic chloride (in order to furnish a tangible residue). The residue should be burnt and analysed in the usual way, and the average amounts of carbon and nitrogen thus obtained deducted from the results of all analyses. This correction, which may be about 0.00035 gm. of C., and 0.00005 gm. of N, includes the errors due to imperfections of the vacuum produced by the Sprengel pump, nitrogen retained in the cupric oxide, ammonia absorbed from the atmosphere during evaporation, &c.

When the quantity of ammonia exceeds 0.009 pts. per 100,000, there is a certain amount of loss of nitrogen during the evaporation by dissipation of ammonia. This appears to be very constant, and is given in Table 3, which has been kindly furnished by Dr Frankland. The number in this table corresponding to the quantity of NH_3 present in the water analysed should be added to the amount of N found by combustion. The number thus obtained includes the nitrogen as ammonia, and this must be deducted to ascertain the *organic* nitrogen.

When, in operating upon sewage, hydric metaphosphate has been employed, Table 4, should be used.

Rules for Converting Parts per 100,000 into Grains per Gallon, or the reverse.

To convert parts per 100,000 into grains per gallon, multiply by 0.7.

To convert grains per gallon into parts per 100,000, divide by 0.7.

To convert grammes per litre into grains per gallon, multiply by 70.

TABLE 1.

Elasticity of Aqueous Vapour for each $\frac{1}{10}$ th degree centigrade from 0° to 30° C. (Regnault).

Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.
0	4.6	6.0	7.0	12.0	10.5	18.0	15.4	24.0	22.2
.1	4.6	.1	7.0	.1	10.5	.1	15.5	.1	22.3
.2	4.7	.2	7.1	.2	10.6	.2	15.6	.2	22.5
.3	4.7	.3	7.1	.3	10.7	.3	15.7	.3	22.6
.4	4.7	.4	7.2	.4	10.7	.4	15.7	.4	22.7
.5	4.8	.5	7.2	.5	10.8	.5	15.8	.5	22.9
.6	4.8	.6	7.3	.6	10.9	.6	15.9	.6	23.0
.7	4.8	.7	7.3	.7	10.9	.7	16.0	.7	23.1
.8	4.9	.8	7.4	.8	11.0	.8	16.1	.8	23.3
.9	4.9	.9	7.4	.9	11.1	.9	16.2	.9	23.4
1.0	4.9	7.0	7.5	13.0	11.2	19.0	16.3	25.0	23.5
.1	5.0	.1	7.5	.1	11.2	.1	16.4	.1	23.7
.2	5.0	.2	7.6	.2	11.3	.2	16.6	.2	23.8
.3	5.0	.3	7.6	.3	11.4	.3	16.7	.3	24.0
.4	5.1	.4	7.7	.4	11.5	.4	16.8	.4	24.1
.5	5.1	.5	7.8	.5	11.5	.5	16.9	.5	24.3
.6	5.2	.6	7.8	.6	11.6	.6	17.0	.6	24.4
.7	5.2	.7	7.9	.7	11.7	.7	17.1	.7	24.6
.8	5.2	.8	7.9	.8	11.8	.8	17.2	.8	24.7
.9	5.3	.9	8.0	.9	11.8	.9	17.3	.9	24.8
2.0	5.3	8.0	8.0	14.0	11.9	20.0	17.4	26.0	25.0
.1	5.3	.1	8.1	.1	12.0	.1	17.5	.1	25.1
.2	5.4	.2	8.1	.2	12.1	.2	17.6	.2	25.3
.3	5.4	.3	8.2	.3	12.1	.3	17.7	.3	25.4
.4	5.5	.4	8.2	.4	12.2	.4	17.8	.4	25.6
.5	5.5	.5	8.3	.5	12.3	.5	17.9	.5	25.7
.6	5.5	.6	8.3	.6	12.4	.6	18.0	.6	25.9
.7	5.6	.7	8.4	.7	12.5	.7	18.2	.7	26.0
.8	5.6	.8	8.5	.8	12.5	.8	18.3	.8	26.2
.9	5.6	.9	8.5	.9	12.6	.9	18.4	.9	26.4
3.0	5.7	9.0	8.6	15.0	12.7	21.0	18.5	27.0	26.5
.1	5.7	.1	8.6	.1	12.8	.1	18.6	.1	26.7
.2	5.8	.2	8.7	.2	12.9	.2	18.7	.2	26.8
.3	5.8	.3	8.7	.3	12.9	.3	18.8	.3	27.0
.4	5.8	.4	8.8	.4	13.0	.4	19.0	.4	27.1
.5	5.9	.5	8.9	.5	13.1	.5	19.1	.5	27.3
.6	5.9	.6	8.9	.6	13.2	.6	19.2	.6	27.5
.7	6.0	.7	9.0	.7	13.3	.7	19.3	.7	27.6
.8	6.0	.8	9.0	.8	13.4	.8	19.4	.8	27.8
.9	6.1	.9	9.1	.9	13.5	.9	19.5	.9	27.9
4.0	6.1	10.0	9.2	16.0	13.5	22.0	19.7	28.0	28.1
.1	6.1	.1	9.2	.1	13.6	.1	19.8	.1	28.3
.2	6.2	.2	9.3	.2	13.7	.2	19.9	.2	28.4
.3	6.2	.3	9.3	.3	13.8	.3	20.0	.3	28.6
.4	6.3	.4	9.4	.4	13.9	.4	20.1	.4	28.8
.5	6.3	.5	9.5	.5	14.0	.5	20.3	.5	28.9
.6	6.4	.6	9.5	.6	14.1	.6	20.4	.6	29.1
.7	6.4	.7	9.6	.7	14.2	.7	20.5	.7	29.3
.8	6.4	.8	9.7	.8	14.2	.8	20.6	.8	29.4
.9	6.5	.9	9.7	.9	14.3	.9	20.8	.9	29.6
5.0	6.5	11.0	9.8	17.0	14.4	23.0	20.9	29.0	29.8
.1	6.6	.1	9.9	.1	14.5	.1	21.0	.1	30.0
.2	6.6	.2	9.9	.2	14.6	.2	21.1	.2	30.1
.3	6.7	.3	10.0	.3	14.7	.3	21.3	.3	30.3
.4	6.7	.4	10.1	.4	14.8	.4	21.4	.4	30.5
.5	6.8	.5	10.1	.5	14.9	.5	21.5	.5	30.7
.6	6.8	.6	10.2	.6	15.0	.6	21.7	.6	30.8
.7	6.9	.7	10.3	.7	15.1	.7	21.8	.7	31.0
.8	6.9	.8	10.3	.8	15.2	.8	21.9	.8	31.2
.9	7.0	.9	10.4	.9	15.3	.9	22.1	.9	31.4

TABLE 2.

Reduction of Cubic Centimetres of Nitrogen to Grammes.

Log. $\frac{0.0012562}{(1+0.00367t)760}$ for each tenth of a degree from 0° to 30°. C.

t. C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0°	6̄.21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	035	020	004	*989	*973	*957	*942	*926	*911	*895
6	6̄.20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	6̄.19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	6̄.18897	882	867	852	837	822*	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	422	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	6̄.17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

TABLE 3.

Parts in 100,000. Loss of Nitrogen by Evaporation of NH_3 .
[SOHo^2 .]

NH_3 .	Loss of N.	NH_3 .	Loss of N.	NH_3 .	Loss of N.	NH_3 .	Loss of N.	NH_3 .	Loss of N.	NH_3 .	Loss of N.
6.0	1.727	4.8	1.451	3.6	.977	2.4	.503	1.2	.250	.09	.014
5.9	1.707	4.7	1.411	3.5	.937	2.3	.463	1.1	.238	.08	.013
5.8	1.688	4.6	1.372	3.4	.898	2.2	.424	1.0	.226	.07	.012
5.7	1.668	4.5	1.332	3.3	.858	2.1	.384	.9	.196	.06	.010
5.6	1.648	4.4	1.293	3.2	.819	2.0	.345	.8	.166	.05	.009
5.5	1.628	4.3	1.253	3.1	.779	1.9	.333	.7	.136	.04	.007
5.4	1.609	4.2	1.214	3.0	.740	1.8	.321	.6	.106	.03	.006
5.3	1.589	4.1	1.174	2.9	.700	1.7	.309	.5	.077	.02	.004
5.2	1.569	4.0	1.135	2.8	.661	1.6	.297	.4	.062	.01	.003
5.1	1.549	3.9	1.095	2.7	.621	1.5	.285	.3	.047	.009	.001
5.0	1.530	3.8	1.056	2.6	.582	1.4	.274	.2	.032
4.9	1.490	3.7	1.016	2.5	.542	1.3	.262	.1	.017

TABLE 4.

Loss of Nitrogen by evaporation of NH_3 . [PO^2Ho .]

Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.
100 c.c.	10.0	.483	100 c.c.	7.2	.386	100 c.c.	4.4	0.283	100 c.c.	1.6	.143
...	9.9	.480	...	7.1	.382	...	4.3	0.279	...	1.5	.137
...	9.8	.476	...	7.0	.379	...	4.2	0.275	...	1.4	.132
...	9.7	.473	...	6.9	.375	...	4.1	0.271	...	1.3	.127
...	9.6	.469	...	6.8	.372	...	4.0	0.267	...	1.2	.122
...	9.5	.466	...	6.7	.368	...	3.9	0.262	...	1.1	.117
...	9.4	.462	...	6.6	.365	...	3.8	0.257	...	1.0	.112
...	9.3	.459	...	6.5	.361	...	3.7	0.252	250 c.c.	0.9	.096
...	9.2	.455	...	6.4	.358	...	3.6	0.247	...	0.8	.080
...	9.1	.452	...	6.3	.354	...	3.5	0.242	...	0.7	.070
...	9.0	.448	...	6.2	.351	...	3.4	0.236	...	0.6	.060
...	8.9	.445	...	6.1	.348	...	3.3	0.231	500 c.c.	0.5	.050
...	8.8	.441	...	6.0	.345	...	3.2	0.226	...	0.4	.040
...	8.7	.438	...	5.9	.341	...	3.1	0.221	...	0.3	.030
...	8.6	.434	...	5.8	.337	...	3.0	0.216	1000 c.c.	0.2	.020
...	8.5	.431	...	5.7	.333	...	2.9	0.211	...	0.1	.010
...	8.4	.428	...	5.6	.330	...	2.8	0.205	...	0.09	.009
...	8.3	.424	...	5.5	.326	...	2.7	0.200	...	0.08	.008
...	8.2	.421	...	5.4	.322	...	2.6	0.195	...	0.07	.007
...	8.1	.417	...	5.3	.318	...	2.5	0.190	...	0.06	.006
...	8.0	.414	...	5.2	.314	...	2.4	0.184	...	0.05	.005
...	7.9	.410	...	5.1	.310	...	2.3	0.179	...	0.04	.004
...	7.8	.407	...	5.0	.306	...	2.2	0.174	...	0.03	.003
...	7.7	.403	...	4.9	.302	...	2.1	0.169	...	0.02	.002
...	7.6	.400	...	4.8	.298	...	2.0	0.164	...	0.01	.001
...	7.5	.396	...	4.7	.294	...	1.9	0.158
...	7.4	.393	...	4.6	.291	...	1.8	0.153
...	7.3	.389	...	4.5	.287	...	1.7	0.148

5. Estimation of Total Solid Matter.

Evaporate over a steam or water bath half a litre or a less quantity of the water in a platinum dish which has been heated to redness and carefully weighed. The water should be filtered or unfiltered, according to the decision made in that respect at the commencement of the analysis. The quantity to be taken is regulated chiefly by the amount of nitrate present, as the residue from this operation is, with certain exceptions, employed for the determination of the nitrogen as nitrates and nitrites. As a general rule, for water supplies and river water half a litre should be used; for shallow well waters, a quarter of a litre. Of sewages, 100 c.c., and of waters containing more than 0.1 pt. of NH^3 & 100,000, a quarter of a litre will generally be convenient, as in these cases the residue will not be used for the estimation of nitrogen as nitrates and nitrites; and therefore the only point to be considered is to have a quantity of residue suitable to weigh. It is desirable to support the platinum dish during evaporation in a glass ring with a flange, shaped like the top of a beaker, the cylindrical part being about 20 m.m. deep. This is dropped into the metal ring on the water bath, and thus lines the metal with glass and keeps the dish clean. A glass disc with a hole in it to receive the dish is not satisfactory, as drops of water conveying solid matter find their way across the under surface from the metal vessel to the dish, and thus soil it. As soon as the evaporation is complete, the dish with the residue is removed, its outer side wiped dry with a cloth, and it is dried in a water or steam oven for about three hours. It is then removed to a desiccator, allowed to cool, weighed as rapidly as possible, returned to the oven and weighed at intervals of an hour, until between two successive weighings it has lost less than 0.001 gm.

6. Estimation of Nitrogen as Nitrates and Nitrites.

The residue obtained in the preceding operation may be used for this estimation. Treat it with about 30 c.c. of hot distilled water, taking care to submit the whole to its action. Add solution of argentic sulphate (C. a.) until the chlorine is entirely precipitated, and heat on the steam bath for a few minutes. Then filter through a very small filter of Swedish paper, washing the dish several times with small quantities of hot distilled water.

It is advisable to rub the dish gently with the finger, so as to detach the solid matter as far as possible, and thus expose it

thoroughly to the action of the water. The finger should be protected by a caoutchouc finger stall, or it will be stained by the silver. Test the filtrate with a drop of argentic sulphate to ascertain if the whole of the chlorine has been precipitated. This may be known before filtration, as a rule, by the residue becoming dark brown whilst on the steam bath. The platinum dish is readily cleaned by immersing it in dilute sulphuric acid, and placing in contact with it a piece of zinc. In a few minutes the argentic chloride present is reduced to the metallic state, and may be entirely dissolved by warm nitric acid. This acid should be kept for this purpose until highly charged with argentic nitrate, and the silver then recovered from it.



Fig. 34.

The filtrate must be evaporated, in a very small beaker, over a steam bath, until reduced to about 1 c.c., or even to dryness. This concentrated solution is introduced into the glass tube shown in fig. 34, standing in the porcelain mercury trough, filled up to the stopcock with mercury. The tube is 210 m.m. in total length, and 15 m.m. in internal diameter. By pouring the liquid into the cup at the top, and then cautiously opening the stopcock, it may be run into the tube without admitting any air. The beaker is rinsed once with a very little hot distilled water, and then two or three times with strong sulphuric acid (*C. β.*), the volume of acid being to that of the aqueous solution about as 3 : 2. The total volume of acid and water should be about 6 c.c. Should any air by chance be admitted at this stage, it may readily be removed by suction, the lips being applied to the cup. With care there is but little danger of getting acid into the mouth.

In a few cases carbonic anhydride is given off on addition of sulphuric acid, and must be sucked out before proceeding.

Now grasp the tube firmly in the hand, closing the open end by the thumb, which should be first moistened; withdraw it from the trough, incline it at an angle of 45° , the cup pointing from you, and shake it briskly with a rapid motion in the direction of its length, so as to throw the mercury up towards the stopcock. After a very little practice there is no danger of the acid finding its way down to the thumb, the mixture of acid and mercury being confined to a comparatively small portion of the tube. In a few seconds some of the mercury becomes very finely divided; and if nitrates be present, in

about a minute or less, nitric oxide is evolved, exerting a strong pressure on the thumb. Mercury is allowed to escape as the reaction proceeds, by partially, but not wholly, relaxing the pressure of the thumb. A slight excess of pressure should be maintained within the tube to prevent entrance of air during the agitation, which must be continued until no more gas is evolved.

When the quantity of nitrate is very large, the mercury, on shaking, breaks up into irregular masses, which adhere to one another as if alloyed with lead or tin, and the whole forms a stiff dark-coloured paste, which it is sometimes very difficult to shake, but nitric oxide is not evolved for a considerable time, then comes off slowly, and afterwards with very great rapidity. To have room for the gas evolved, the operator should endeavour to shake the tube so as to employ as little as possible of the contained mercury in the reaction. At the close of the operation the finely-divided mercury will consist for the most part of minute spheres, the alloyed appearance being entirely gone. An experiment with a large quantity of nitrate may often be saved from loss by firmly resisting the escape of mercury, shaking until it is judged by the appearance of the contents of the tube that the reaction is complete, and then on restoring the tube to the mercury trough, allowing the finely-divided mercury also to escape in part. If the gas evolved be not more than the tube will hold, and there be no odour of pernitric oxide from the escaped finely-divided mercury, the operation may be considered successful. If the amount of nitrate be too large, a smaller quantity of the water must be evaporated and the operation repeated. When no nitrate is present, the mercury usually manifests very little tendency to become divided, that which does so remains bright, and the acid liquid does not become so turbid as it does in other cases.

The reaction completed, the tube is taken up covered by the thumb, and the gas is decanted into the laboratory vessel, and measured in the usual way in the gas apparatus. The nitric acid tube is of such a length, that when the cup is in contact with the end of the mercury trough, the open end is just under the centre of the laboratory vessel. If any acid has been expelled from the tube at the close of the shaking operation, the end of the tube and the thumb should be washed with water before introducing into the mercury trough of the gas apparatus, so as to remove any acid which may be adhering, which would destroy the wood of the trough.

As nitric oxide contains half its volume of nitrogen, if half a litre

of water has been employed, the volume of nitric oxide obtained will be equal to the volume of *nitrogen* present as nitrates and nitrites in one litre of the water, and the weight of the nitrogen may be calculated as directed in the paragraph on the estimation of organic carbon and nitrogen.

When more than 0.1 of ammonia is present in 100,000 parts of liquid, there is danger of loss of nitrogen by decomposition of ammoniac nitrite on evaporation; and therefore the residue from the estimation of total solid matter cannot be used. In such cases acidify a fresh quantity of the liquid with dilute hydric sulphate, add solution of potassic permanganate, a little at a time, until the pink colour remains for about a minute, and render the liquid just alkaline to litmus paper with sodic carbonate. The nitrites present will then be converted into nitrates, and may be evaporated without fear of loss. Use as little of each re-agent as possible. Sewage may be examined in this way; but it is hardly necessary to attempt the determination, as sewage is almost invariably free from nitrates and nitrites. Out of several hundred specimens, the writer only found two or three which contained any, and even then only in very small quantity.

7. Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, with but little Ammonia or Organic Nitrogen.

When the quantity of soluble matter is excessive, as, for example, in sea-water, the preceding method is inapplicable, as the solution to be employed cannot be reduced to a sufficiently small bulk to go into the shaking tube. If the quantity of organic nitrogen be less than 0.1 part in 100,000, the nitrogen as nitrates and nitrites may generally be determined by the following modification of Schulze's method, devised by E. T. Chapman. To 200 c.c. of the water add 10 c.c. of sodic hydrate solution (C. ζ.), and boil briskly in an open porcelain dish until it is reduced to about 70 c.c. When cold pour the residue into a tall glass cylinder of about 120 c.c. capacity, and rinse the dish with water free from ammonia. Add a piece of aluminium foil of about 15 sq. centim. area, loading it with a piece of clean glass rod to keep it from floating. Close the mouth of the cylinder with a cork, bearing a small tube filled with pumice (C. η.) moistened with hydric chloride free from ammonia (C. θ.)

Hydrogen will speedily be given off from the surface of the aluminium, and in five or six hours the whole of the nitrogen as

nitrates and nitrites, will be converted into ammonia. Transfer to a small retort the contents of the cylinder, together with the pumice, washing the whole apparatus with a little water free from ammonia. Distil, and estimate ammonia in the usual way with Nessler solution. It appears impossible wholly to exclude ammonia from the re-agents and apparatus, and therefore some blank experiments should be made to ascertain the correction to be applied for this. This correction is very small, and appears to be nearly constant.

8. Estimation of Suspended Matter.

Filters of Swedish paper, about 110 m.m. in diameter, are moistened with dilute hydrochloric acid, washed with distilled water until the washings cease to contain chlorine, and dried. The ash of the paper is thus reduced by about 60 per cent., and must be determined for each parcel of filter paper by incinerating 10 filters, and weighing the residue. For use in estimating suspended matter, these washed filters must be dried for several hours at 120–130° C., and each one then weighed at intervals of an hour until the weight ceases to diminish. It is most convenient to enclose the filter during weighing in two short tubes fitting closely one into the other. The closed ends of test tubes, 50 m.m. long, cut off by leading a crack round with the aid of a pastille or very small gas jet, the sharp edges being afterwards fused at the blowpipe, answer perfectly. In the air-bath they should rest in grooves formed by a folded sheet of paper, the tubes being drawn apart, and the filter almost, but not quite, out of the smaller tube. They can then be shut up whilst hot by gently pushing the tubes together, being guided by the grooved paper. They require about twenty minutes in a dessicator to cool before weighing. Filtration will be much accelerated if the filters be ribbed before drying. As a general rule, it will be sufficient to filter a quarter of a litre of a sewage, half a litre of a highly polluted river, and a litre of a less polluted water; but this must be frequently varied to suit individual cases. Filtration is hastened, and trouble diminished, by putting the liquid to be filtered into a narrow-necked flask, which is inverted into the filter. With a little practice this may be done without loss, and without previously closing the mouth of the flask. When all has passed through, the flask should be rinsed out with distilled water, and the rinsings added to the filter. Thus any particles of solid matter left in the flask are secured, and the mother

liquor adhering to the filter is displaced. The filtrate from the washings should not be added to the previous filtrate, which may be employed for determination of total solid matter, chlorine, hardness, &c.

Thus washed, the filter with the matter upon it is dried in the steam oven, then transferred from the funnel to the same pair of tubes in which it was previously weighed, and the operation of drying at 120° – 130° C. and weighing until constant repeated. The weight thus obtained, minus the weight of the empty filter and tubes, gives the weight of the total suspended matter dried at 120° – 130° C.

To ascertain the quantity of mineral matter in this, the filter with its contents is incinerated in a platinum crucible, and the total ash thus determined, minus the ash of the filter alone, gives the weight of the mineral suspended matter.

9. Estimation of Chlorine present as Chloride.

To 50 c.c. of the water add two or three drops of solution of potassic chromate (**D. β .**), so as to give it a faint tinge of yellow, and add gradually from a burette standard solution of argentic nitrate (**D. α .**), until the red argentic chromate which forms after each addition of the nitrate ceases to disappear on shaking. The number of c.c. of silver solution employed will express the chlorine present as chloride in parts in 100,000. If this amount be much more than 10, it is advisable to take a smaller quantity of water.

If extreme accuracy be necessary, after completing a determination, destroy the slight red tint by an excess of a soluble chloride, and repeat the estimation on a fresh quantity of the water in a similar flask placed by the side of the former. By comparing the contents of the flasks, the first tinge of red in the second flask may be detected with great accuracy. It is absolutely necessary that the liquor examined should not be acid, unless with carbonic acid, nor more than very slightly alkaline. It must also be colourless, or nearly so. These conditions are generally found in waters, but, if not, they may be brought about in most cases by rendering the liquid just alkaline with lime water (free from chlorine), passing carbonic anhydride to saturation, boiling, and filtering. The calcic carbonate has a powerful clarifying action, and the excess of alkali is neutralised exactly by the carbonic anhydride. If this is not successful, the water must be rendered alkaline, evaporated to dryness, and the residue gently heated to destroy organic matter. The

chlorine may then be extracted with water, and estimated in the ordinary way, either gravimetrically or volumetrically.

10. Estimation of Hardness.

The following method, devised by the late Dr Thomas Clark of Aberdeen, is in general use; and from its ease, rapidity, and accuracy, is of great value.

Uniformity in conducting it is of great importance; especially, the titration of the soap solution, and the estimation of the hardness of waters, should be performed in precisely similar ways.

Measure 50 c.c. of the water into a well-stoppered bottle of about 250 c.c. capacity, shake briskly for a few seconds, and suck the air from the bottle by means of a glass tube, in order to remove any carbonic anhydride which may have been liberated from the water. Add standard soap solution (*E. β.*) from a burette, one c.c. at a time at first, and smaller quantities towards the end of the operation, shaking well after each addition, until a soft lather is obtained, which, if the bottle is placed at rest on its side, remains continuous over the whole surface for five minutes. The soap should not be added in larger quantities at a time, even when the volume required is approximately known.

When more than 16 c.c. of soap solution are required by 50 c.c. of the water, a less quantity (as 25 or 10 c.c.) of the latter should be taken, and made up to 50 c.c. with recently boiled distilled water, so that less than 16 c.c. of soap solution will suffice, and the number expressing the hardness of the diluted water multiplied by 2 or 5, as the case may be.

When the water contains much magnesium, which may be known by the lather having a peculiar curdy appearance, it should be diluted, if necessary, with distilled water, until less than 7 c.c. are required by 50 c.c.

The volume of standard soap solution required for 50 c.c. of the water being known, the weight of calcic carbonate (Ca CO_3) corresponding to this may be ascertained from the following table:*

* The table is calculated from that originally constructed by Dr Clark, which is as follows:—

Degree of Hardness.	Measures of Soap Solution.	Differences for the next 1° of hardness.
0° (Distilled water),	1·4	1·8
1	3·2	2·2
2	5·4	2·2
3	7·6	2·0

When water containing calcic and magnesian carbonates, held in solution by carbonic acid, is boiled, carbonic anhydride is expelled and the carbonates precipitated. The hardness due to these is said to be *temporary*, whilst that due to sulphates, chlorides, etc., and to the amount of carbonates soluble in pure water (*i.e.* about three parts per 100,000), is called *permanent*.

To estimate permanent hardness, a known quantity of the water is boiled gently for half-an-hour in a flask, on the mouth of which stands a vertical glass tube, about 1 metre in length, and 5 m.m. internal diameter, having a bulb blown on its lower end, which rests on the mouth of the flask. This tube condenses and returns a large

Degree of Hardness.	Measures of Soap Solution.	Differences for the next 1° of hardness.
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	1·9
8	17·5	1·9
9	19·4	1·9
10	21·3	1·8
11	23·1	1·8
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	—

Each “measure” being 10 grains, the volume of water employed 1000 grains, and each degree 1 grain of calcic carbonate in a gallon.

If the old weights and measures, grains and gallons, be preferred, this table may be used, the process being exactly as above described, but 1000 grains of water taken instead of 50 c.c., and the soap solution measured in 10 grain measures instead of cubic centimetres. If the volume of soap solution used be found exactly in the second column of the table, the hardness will, of course, be that shown on the same line in the first column. But if it be not, deduct from it the next lower number in the second column, when the corresponding degree of hardness in the first column will give the integral part of the result; divide the remainder by the difference on the same line in the third column, and the quotient will give the fractional part. For example, if 1000 grains of water require 16 “measures” of soap, the calculation will be as follows:—

$$\begin{array}{r}
 16 \cdot 0 \\
 - 15 \cdot 6 \text{ (= } 7^\circ \text{ hardness).} \\
 \hline
 \text{(Difference =)} \quad 1 \cdot 9) \quad \cdot 4 \\
 \hline
 \cdot 21
 \end{array}$$

therefore the hardness is 7·21 grains of Ca CO₃ per gallon. The water must be diluted, if necessary, so that the quantity of soap required does not exceed 32 measures in ordinary water, and 14 measures in waters containing much magnesium.

proportion of the water, which is driven off as steam. At the end of the boiling, the water should be allowed to cool, and the original weight made up by adding distilled water.

Much trouble may be avoided by using flasks of about the same weight, and taking so much water in each as will make up the same uniform weight. Thus, if all the flasks employed weigh less than 50 gms. each, let each flask with its contents be made to weigh 200 gms.

After boiling and making up to the original weight, filter the water, and determine the hardness in the usual way. The hardness thus found, deducted from that of the unboiled water, will give the *temporary* hardness.

The quantities of the following substances which may be present in a sample of water are subject to such great variations that no definite directions can be given as to the volume of water to be used. The analyst must judge in each case from a preliminary experiment what will be a convenient quantity to take.

11. Sulphuric Acid.

Acidify a litre or less of the water with hydrochloric acid, concentrate on the water bath to about 100 c.c., and while still hot add a slight excess of baric chloride. Filter, wash, ignite, and weigh as baric sulphate, or estimate volumetrically as in § 38.

12. Hydric Sulphide.

Titrate with a standard solution of iodine in potassic iodide, with starch as an indicator, as in § 31.

13. Phosphoric Acid.

Acidify a litre or more of the water with nitric acid, concentrate to a small bulk, and add a large excess of a solution of ammonic molybdate with a large proportion of nitric acid. Allow to stand for 24 hours in a warm place, filter, dissolve the precipitate in ammonia, precipitate with magnesian sulphate, and weigh as magnesian pyrophosphate, or if the quantity is large, it may be estimated volumetrically, as in § 80.

14. Silicic Acid.

Acidify a litre or more of the water with hydrochloric acid, evaporate, and dry the residue thoroughly. Then moisten with hydro-

chloric acid, dilute with hot water, and filter off, wash, ignite, and weigh the silica separated.

15. Iron.

To the filtrate from the estimation of silicic acid add a few drops of nitric acid, and concentrate to a small bulk ; add excess of ammonia, and heat gently for a short time. Filter off the precipitate, and weigh as ferric oxide, or estimate the iron in the washed precipitate volumetrically, as in § 27.

16. Calcium.

To the filtrate from the iron estimation add excess of ammonic oxalate, filter off the calcic oxalate, and weigh as calcic carbonate.

17. Magnesium.

To the filtrate from the calcium estimation add sodic phosphate (or, if alkalies are to be determined in the filtrate, ammonic phosphate), and allow to stand for 24 hours in a warm place. Filter, ignite the precipitate, and weigh as magnesian pyrophosphate.

18. Potassium and Sodium.

These are generally determined jointly, and for this purpose the filtrate from the magnesium estimation may be used. Evaporate to dryness, and heat gently to expel ammonium salts, remove phosphoric acid with plumbic acetate, and the excess of lead in the hot solution by ammonia and ammonic carbonate. Filter, evaporate to dryness, heat to expel ammonium salts, and weigh the alkalies as chlorides.

It is, however, generally less trouble to employ a separate portion of water. Add to a litre or less of the water enough pure baric chloride to precipitate the sulphuric acid, boil with pure milk of lime, filter, concentrate, and remove the excess of lime with ammonic carbonate and a little oxalate. Filter, and weigh the alkaline chlorides in the filtrate. If the water contains but little sulphate, the baric chloride may be omitted, and a little ammonic chloride added to the solution of alkaline chlorides.

If potassium and sodium must each be estimated, separate them by means of platinic chloride ; or, after weighing the mixed chlorides, determine the *chlorine* present in them, and calculate the amounts of potassium and sodium by the following formula :—Calculate all the chlorine present as potassic chloride ; deduct this from the

weight of the mixed chlorides, and call the difference d . Then as $16.1 : 58.5 :: d : \text{NaCl present}$.

19. Lead.

May be estimated by the method proposed by the late Dr Miller. Acidulate the water with two or three drops of acetic acid, and add $\frac{1}{20}$ of its bulk of saturated aqueous solution of sulphuretted hydrogen. Compare the colour thus produced in a convenient cylinder with that obtained with a known quantity of a standard solution of a lead salt, in a manner similar to that described for the ammonia estimation. The lead solution contains 0.1831 gm. of normal crystallised plumbic acetate in a litre of distilled water, and therefore each c.c. contains 0.0001 gm. of metallic lead.

20. Arsenic.

Add to half a litre or more of the water enough sodic hydrate, free from arsenic, to render it just alkaline, evaporate to dryness, and extract with a little concentrated hydrochloric acid. Introduce this solution into the generating flask of a small Marsh's apparatus, and pass the evolved hydrogen, first through a U-tube filled with pumice, moistened with plumbic acetate, and then through a piece of hard glass tube about 150 m.m. in length, and 3 m.m. in diameter (made by drawing out combustion tube). At about its middle, this tube is heated to redness for a length of about 20 m.m. by a small gas flame, and here the arsenetted hydrogen is decomposed, arsenic being deposited as a mirror on the cold part of the tube. The mirror obtained after the gas has passed slowly for an hour is compared with a series of standard mirrors obtained in a similar way with known quantities of arsenic. Care must be taken to ascertain in each experiment that the hydrochloric acid, zinc, and whole apparatus is free from arsenic, by passing the hydrogen slowly through the heated tube before introducing the solution to be tested.

THE INTERPRETATION OF THE RESULTS OF ANALYSIS.

§ 84. It is impossible to give any fixed rules by which the results obtained by the foregoing method of analysis should be interpreted. The analyst must form an independent opinion for each sample from a consideration of all the results he has obtained. Nevertheless, the following remarks, illustrated by reference to the twelve analyses given in the accompanying table, will probably be of service.

TABLE 6.
Results of Analysis expressed in parts per 100,000.

Source of Water.	Total Solid Matter.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage Contamination.	Organic $\frac{C}{N}$	Suspended Matter.			Chlorine.	Hardness.		
									Mineral.	Organic.	Total.		Temporary.	Permanent.	Total.
I. London Water Supply—Southwark Co., ave., 1870,	26·19	·160	·024	0	·206	·230	1740	6·67	...	Clear	...	1·68	20·34
II. London Water Supply—New River Co., ave., 1870,	26·43	·087	·015	0	·247	·262	2150	5·8	...	Clear	...	1·52	20·82
III. Whitehaven Water Supply, Sept. 28, 1868,	2·16	·042	·017	0	0	·017	0	2·47	...	Clear	...	·99	0	1·45	1·45
IV. River Leam above the Sewage Works, May 10, 1870,	74·80	·499	·061	·040	·178	·272	1790	8·18	3·48	15·55	12·51	28·06
V. River Medlock near its Source, July 22, 1868,	12·80	·166	·014	·004	·011	·028	0	11·86	...	Clear	...	1·29	·92	6·04	6·96
VI. River Medlock at Manchester, June 17, 1868,	57·00	1·776	·743	1·660	0	2·115	...	2·37	10·90	7·86	18·76	10·82	15·55	5·43	20·98
VII. Pillory Pump, Bedford, Oct. 10, 1868,	140·74	·325	·088	0	2·497	2·585	24650	3·69	...	Clear	...	15·29	29·11	25·40	54·51
VIII. Artesian Well, Trafalgar Square, May 6, 1869,	83·40	·150	·012	·070	0	·070	260	12·50	...	Clear	...	16·55	2·97	2·95	5·92
IX. London Sewage, average, Feb.-June, 1869,	64·50	4·386	2·484	5·557	0	7·060	...	1·77	42·46	27·04	69·50	10·37
X. Salford Sewage, Wooden Street Sewer, March 15, 1869,	419·60	11·012	7·634	6·640	0	13·102	...	1·44	18·88	26·44	45·32	20·50
XI. Lancaster Sewage, Sept. 30, 1868,	39·80	1·854	·357	1·600	0	1·675	...	5·19	19·48	7·64	27·12
XII. Bradford Beck, below Bradford, Oct. 5, 1869,	75·50	4·024	·392	1·220	0	1·397	...	10·27	15·95	36·05	52·00	5·45	10·76	13·75	24·51

These may be considered as fairly typical samples.

Total Solid Matter.

This estimation is chiefly of importance as regards the use of the water for steam boilers, as the amount of incrustation produced will chiefly depend upon it. It may vary considerably, independently of any unnatural pollution of the water, as it depends chiefly on the nature of the soil through and over which it passes. River water, which is but slightly polluted, contains generally from 10 to 25 parts, and sewage from 50 to 100, so that X. in the table contains an exceptionally large, and XI. an exceptionally small quantity. Shallow well water varies greatly, containing from 30 parts to 150, or even more. The total solid matter, as a rule, exceeds the sum of the constituents determined; the nitrogen as nitrates and nitrites being calculated as potassic nitrate, and the chlorine as sodic chloride; but occasionally this is not the case, owing, it is likely, to the presence of some of the calcium as calcic nitrate or chloride.

Organic Carbon and Nitrogen.

The existing condition of the sample, as far as organic contamination is concerned, must be inferred from the amount of these two constituents. In a good water, suitable for domestic supply, the former should not, under ordinary circumstances, much exceed 0.2 and the latter 0.02 parts. When the quantities exceed 2.0 and 0.5 parts respectively, the sample may be considered as belonging to the class of sewages, the intermediate quantities indicating various degrees of present pollution. In the table above, XI. is a very weak, and X. a very strong sewage; an average sewage would contain about four parts of organic carbon, and two parts of organic nitrogen. The proportion existing between the organic carbon and nitrogen, as seen in the table in the eighth column (which shows the fourth term of the proportion—organic nitrogen : organic carbon :: 1 : x), is of considerable importance. As a rule, the higher this ratio, the less objectionable is the organic matter in the water. In ordinary sewage, it will vary from one to three; in a polluted river water, from three to five; and in a good water, from five to twelve. There are, however, many exceptional cases, especially among very soft waters, which often have a very low ratio; whilst, on the other hand, waters from peaty districts generally have a very high one. It is a curious fact that in sea water the organic nitrogen is generally

slightly *more* than the organic carbon. It appears that during the spontaneous oxidation of the organic matter in water, carbon is more rapidly eliminated as carbonic anhydride than is nitrogen in the form of ammonia or nitrates, hence, as the process goes on, the ratio of C : N becomes lower. It is owing to this circumstance that it is frequently very low in deep spring and deep well waters, the organic constituents of which have been obviously long subjected to oxidising action, and that it is lowest of all in sea water, where the time of oxidation may be regarded as infinite.

When in the case of a water containing much nitrogen as nitrates and nitrites, this ratio is unusually low, incomplete destruction of nitrates during the evaporation may be suspected, and the estimation should be repeated. For this purpose, if a water contain any considerable quantity of ammonia, it is well, when commencing the evaporation in the first instance, to set aside a quantity sufficient for this repetition, adding to it the usual proportion of sulphurous acid.

Ammonia.

All the ammonia found in a water is, with the exception of a minute quantity of atmospheric origin, derived from animal contamination. Its quantity varies between very wide limits. Sewage usually contains from two to six parts, but a few cases have been observed in which the quantity has been as great as nine or ten parts. A moderately polluted river water will contain from 0.01 to 0.2 parts; and an unpolluted river, or a water which has passed through freely aerated porous soil, will generally contain less than 0.01 part. Very deep well waters, however, are exceptions to this rule, as they generally contain a large proportion of ammonia, sometimes as much as 0.1 part.

Nitrogen as Nitrates and Nitrites.

The quantity of nitrogen in this condition in water varies greatly. Water derived from the drainage of thinly inhabited districts, such as the mountains of Wales, Cumberland, and the Highlands of Scotland, will contain none, or but traces. Slightly polluted river waters and water from deep-seated springs contain 0.5 parts or less; while the water of shallow wells may contain as much as five or ten parts, or even a larger quantity, from three to five parts being perhaps most general. Sewage, for reasons which will be given presently, is, for the most part, free from nitrogen in this state.

Total Combined Nitrogen.

The numbers under this heading are obtained by adding together the amounts of nitrogen found as organic nitrogen, as ammonia, and as nitrates and nitrites, and they give relative values for the *minimum* animal contamination which the water has undergone since its descent to the earth as rain; the whole of it having an animal origin, with the exception of the small quantity found in rain water.

Previous Sewage or Animal Contamination.

This column is based on the following considerations:—When animal organic matters undergo decomposition, their nitrogen appears as ammonia, nitrous acid, and nitric acid; the two last combining with the bases in the water to form nitrites and nitrates. All these substances are perfectly innocuous themselves, but show by their presence that the water *has been* contaminated by animal matter. In order to obtain a value for this contamination in a convenient form, it has been suggested by Dr Frankland that it should be expressed in terms of the quantity of average filtered London sewage, which would, when oxidised, yield the same amount of nitrogen in this condition. For this purpose the analyses of Hofmann, Witt, Way, and Odling have been taken, which give in round numbers ten parts of combined nitrogen as the average amount present in 100,000 parts of such sewage. Of course, we might instead merely state the quantity of nitrogen found as ammonia and nitrates and nitrites, but the above method gives numbers which are rather more convenient. As a matter of fact, London sewage at the present time is considerably more dilute than it was when the above analyses were made, but this is of no moment, as the numbers obtained are equally valuable for comparison. From the total amount of nitrogen thus found in the products of decomposition, a quantity corresponding to 0·032 parts in 100,000 must be deducted, on account of the combined nitrogen found in rain water. This is based on numerous analyses by Lawes, Gilbert, and Way, and is the *maximum* amount in such water. To calculate, then, the quantity of this standard filtered London sewage which would contain as much combined nitrogen as is present in the water under examination in the form of ammonia and of nitrates and nitrites, add together the quantities of nitrogen found by these determinations, deduct 0·032 part, and multiply by 10,000.

Previous sewage contamination thus calculated does not, however,

denote *actual* but *potential* evil. It will be seen that the innocuous character of a water showing much *previous* contamination depends wholly on the permanence of the conditions of temperature, filtration through soil, &c., which have broken up the original organic matter; if these should at any time fail, the *previous* contamination would become *present*, the nitrogen appearing in the organic form, the water being loaded in all likelihood with putrescent and contagious matter.

The ammonia in sewage is principally derived from the decomposition of urea and its allies. This may be considered as the first stage of decomposition, but is not a process of oxidation. When sewage is freely exposed to the action of oxygen, the remainder of the organic matter undergoes oxidation, the carbon and hydrogen forming carbonic acid and water, and the nitrogen ammonia, nitric acid, and nitrous acid. At the same time, the ammonia is also oxidised to nitric acid, so that the water resulting from the filtration of sewage through aerated porous soil contains very little organic carbon, organic nitrogen, or ammonia, but a large quantity of nitrates. Such a water is shown in the table in number VII. On the other hand, putrescent matter in the *absence* of free oxygen *reduces* nitrates, so that when sewage is added to a water containing nitrates, after a short time the whole of the nitrates will disappear. Hence sewages very rarely contain nitrates or nitrites. In the same manner, it may happen that a quantity of sewage may be added to a water which is just sufficient to employ the whole of the free oxygen present, and destroy the nitrates, so that addition of *present* sewages frequently obliterates, either partially or totally, the trace of *previous* sewage contamination. This is especially the case in hot weather.

Suspended Matter.

This is of a less degree of importance than the matters hitherto considered. From a sanitary point of view it is of minor interest, because it may be so readily and completely removed by filtration. It is, however, of considerable mechanical importance as regards the formation of impediments in the river bed by its gradual deposition and as regards the choking of the sand filters in water works.

Chlorine.

This is usually present as sodic chloride, but occasionally, as has been mentioned before, it is most likely as a calcic salt. It is derived,

in some cases, from the soil, but more usually from excreta, and is therefore of considerable importance in forming a judgment of the character of a water. Unpolluted river and spring waters usually contain less than one part, average town sewage about ten parts. Shallow well water may contain any quantity from a mere trace up to twenty or even thirty parts. Its amount is scarcely affected by any degree of filtration through soil. Of course, attention should be given to the geological nature of the district from which the water comes, in order to decide on the origin of the chlorine. Water from some parts of Cheshire, for example, would contain a large quantity of chlorine, and yet be quite free from animal contamination.

Hardness.

This is chiefly of importance as regards the use of the water for cleansing and manufacturing purposes, and for steam boilers. It is still a moot point as to whether hard or soft water is better as an article of food. The temporary hardness is often said to be that due to carbonates held in solution by carbonic acid, but this is not quite correct; for even after prolonged boiling, water will still retain about three parts of carbonate in solution, and therefore when the total hardness exceeds three parts, that amount should be deducted from the permanent hardness and added to the temporary, in order to get the quantity of carbonate in solution. But the term "temporary" hardness properly applies to the amount of hardness which may be removed by boiling, and hence, if the total hardness be less than three parts, there is usually no *temporary*. As the hardness depends on the nature of the soil through and over which the water passes, the variations in it are very great. River waters, unless greatly polluted, do not often contain more than thirty parts. No generalisation is possible as to the proportion of permanent to temporary hardness.

From the determinations which have been described, it is believed that a sound judgment of the character of a water may be made, and the analyst should hardly be content with a less complete analysis. If, however, from lack of time or other cause, so much cannot be done, a tolerably safe opinion may be formed, omitting the determination of total solid matter, and organic carbon and nitrogen. But it must not be forgotten that by so doing the inquiry is limited as regards organic impurity to the determination of what has been termed *previous* contamination. If still less must suffice, the estimation of nitrogen as nitrates and nitrites may be omitted, its place

being to a certain extent supplied by the estimation of chlorine, but especial care must then be taken to ascertain its source by examination of the district. If this be in any degree mineral, no opinion can be formed from it as to the likelihood of organic pollution. At best, so slight an examination must be of but little value.

Clark's Process for Softening Hard Water.

The patent right of this process having expired, the public are free to use it.

This method of softening consists in adding lime to the hard water. It is only applicable to water which owes its hardness entirely, or chiefly, to the calcic and magnesian carbonates held in solution by carbonic acid (*temporary hardness*). Water which owes its hardness to calcic or magnesian sulphate (*permanent hardness*) cannot be thus softened, but any water which softens on boiling for half-an-hour will be softened to an equal extent by Clark's process. The hard water derived from chalk, limestone, or oolite districts is generally well adapted for this operation.

To soften 1000 gallons of water, one ounce of quicklime is required for each part of temporary hardness in 100,000 parts of water. The quantity of quicklime required is thoroughly slaked in a pailful of water. Stir up the milk of lime thus obtained and pour it immediately into the cistern containing at least 50 gallons of the water to be softened, taking care to leave in the pail any heavy sediment that may have settled to the bottom in the few seconds that intervened between the stirring and pouring. Fill the pail again with water, and stir and pour as before. The remainder of the 1000 gallons of water must then be added, or allowed to run into the cistern from the supply pipe. If the rush of the water thus added does not thoroughly mix the contents of the cistern, this must be accomplished by stirring with a suitable wooden or iron paddle. The water will now appear very milky, owing to the precipitation of the chalk which it previously contained in solution, together with an equal quantity of chalk which is formed from the quicklime added.

After standing for three hours the water will be sufficiently clear to use for washing, but to render it clear enough for drinking at least twelve hours' settlement is required. This process not only softens water, but it removes to a great extent objectionable organic matter present.

METHODS OF WATER ANALYSIS WITHOUT GAS APPARATUS.

§ 85. THE foregoing methods of estimating the organic impurities in potable waters, though very comprehensive and reliable, yet possess the disadvantage of occupying a good deal of time, and necessitate the use of a complicated and expensive set of apparatus, which may not always be within the reach of the operator.

Nothing of a strictly reliable character as to the nature of the organic matter or its quantity can be gained from the use of standard permanganate solution, and the same remark applies to the loss on ignition of the residue, both of which have been in past time largely used.

We are indebted to Messrs Wanklyn, Chapman, and Smith for an ingenious and novel method of estimating the quantity of nitrogenous organic matter in water, which depends upon the decomposition of such organic matter when distilled with an alkaline solution of potassic permanganate.

The authors have given the term "Albuminoid ammonia" to the NH^3 produced from nitrogenous matter by the action of the permanganate, doubtless because the first experiments made in the process were made with albumin; but the authors also proved that ammonia may be obtained in a similar way from a great variety of nitrogenous organic substances, such as hippuric acid, narcotine, strychnine, morphine, creatine, gelatine, &c. Unfortunately, however, although the proportion of nitrogen yielded by any one substance when treated with boiling alkaline permanganate appears to be definite, yet different substances give different proportions of their nitrogen. Thus hippuric acid and narcotine yield the whole, but strychnine and morphine only one-half of their known proportion of nitrogen. Hence the value of the numerical results thus obtained depends entirely on the assumption that the nitrogenous organic matter in water is *uniform in its nature*, and the authors say that in a river polluted mainly by sewage "the disintegrating animal refuse would be pretty fairly measured by ten times the albuminoid ammonia which it yields."

It is stated that the albuminoid ammonia from a good drinking water should not exceed 0.008 parts in 100,000. The average in fifteen samples of Thames water supplied to London by the various Water Companies in 1867 was 0.0089, and in five samples supplied by the New River Company 0.0068 parts per 100,000.

The rapidity and simplicity of the operation are the great merits of this process, and the information to be obtained from its performance may for some purposes be of considerable value; and even if the numerical results cannot be insisted upon, yet a *good* water could not be condemned by it, and a *bad* one ought certainly not escape it.

The method was first communicated to the Chemical Society in 1867 (Jour. Chem. Soc., N.S., vol. v., p. 591), and a little treatise has since been published (1870) by Messrs Wanklyn and Chapman, describing their general methods of examining water, to which the reader is referred.

Mr Alfred Wanklyn, late Professor of Chemistry in the London Institution, and one of the authors above mentioned, examined several samples of Norwich waters for free and albuminoid ammonia in the author's laboratory in 1868, so that the practical details are familiar to him, and will now be described:—

1. Estimation of Free Ammonia.

This process is conducted precisely as described in § 83.3, and the residue may be used immediately afterward for the estimation of albuminoid ammonia if desired, or both processes may be conducted as described by Wanklyn and Chapman as follows:—

Half a litre of the water is measured into the retort with 15 c.c. of saturated solution of sodic carbonate, and a Bunsen's burner placed close under the bottom of the retort (almost touching it), and lighted full on; the distillation soon commences, and must be received in a tall cylinder holding about 150 c.c., and marked at 50 and 100 c.c. Three or four such cylinders are required at hand during the operation. When 100 c.c. have been distilled, the amount of free ammonia in it is estimated with Nessler solution, precisely as described at page 258, except that to the 100 c.c.— $1\frac{1}{2}$ c.c. of solution is added and well stirred. If the proportion is large, it will be necessary to distil a further 50 or 100 c.c., but, generally speaking, the whole of the free NH_3 will come over in the first 100 or 150 c.c., but in any case the distillation should be continued until 50 c.c. of the distillate contain less than $\frac{1}{100}$ milligramme of NH_3 , which is of course readily ascertained by means of the comparative effects obtained simultaneously upon known solutions of ammonia.

2. Estimation of Albuminoid Ammonia.

To the contents of the retort left from the operation just described, is at once added 50 c.c. of the following solution :—

Potassic permanganate,	8 gm.
Potassic hydrate,	200 gm.
Distilled water,	One litre.

This liquid should be boiled for a short time when made to expel ammonia, and should be tested on a sample of pure water before use, then preserved in a stoppered bottle.

Having added this, resume the distillation, and estimate the ammonia as before until no more is evolved ; generally speaking, it is sufficient to distil 200 c.c. after adding the above liquid, estimating the ammonia in each 100 c.c. The boiling is often very irregular, especially in bad waters, and if so it is advisable to introduce into the retort a few small pieces of freshly ignited pumice to moderate the bumping. It is also frequently necessary to incline the neck of the retort upward, so that the liquid carried up by spirting may be returned as previously mentioned, the rather as manganese compounds in particular, have a powerful effect upon the colour produced by the Nessler solution, greatly intensifying it, and thus vitiating the results. The amount of ammonia estimated by the Nessler test in this distillate is entered as albuminoid ammonia, and the total result of both distillations may be tabulated as follows :—

Half a litre taken.	Milligm. NH ₃ .
1. Distillate from Na CO ³ ,	100 c.c. = 0·015
2. Do. from permanganate,	100 c.c. = 0·035
Do. from „	100 c.c. = 0·015

This particular water therefore contains, per litre—

Free ammonia,	0·03 mgm.
Albuminoid do.,	0·10 mgm.

or in parts per 100,000—

Free ammonia,	0·003
Albuminoid do.,	0·010

3. Nitrogen as Nitrates and Nitrites.

These may be accurately estimated as described at page 277, or a very fair approximate estimation may be rapidly made by adding to 100 c.c. of the water contained in one of the cylinders used for estimation of ammonia 10 c.c. of solution of sodic hydrate (C. ζ.),

and a small piece of aluminium sheet,—as soon as the latter is dissolved, Nessler solution may be added, and an idea of the quantity of nitrates and nitrites obtained. The same quantity of Nessler solution should also be added to 100 c.c. of the water without treatment with sodic hydrate and aluminium, in order to obtain a correction for the quantity of free NH^3 in the water. This method does not, however, answer for some waters, since they produce a deposit rather than a colour with the Nessler test.

4. Estimation of Total Solid Matter.

This is performed as described at page 277. The quantity to be taken for the estimation depends upon the nature of the water, and a fair judgment may be obtained from the appearance of the precipitate in the treatment with sodic carbonate in distilling for free ammonia, or from the hardness.

If only 70 or 100 c.c. are taken for evaporation as recommended by Wanklyn, extreme care and rapidity must be used in cooling and weighing the residue.

5. Estimation of Hardness.

This is performed exactly as described at page 283.

6. Colour and Smell of the Water.

A very tolerable opinion may be formed as to whether a sample of water contains unchanged organic matter by comparing its colour with that of distilled water; to this end two white glass cylinders, about 12 or 18 inches high, should be placed upon white paper or a white porcelain slab, one filled with distilled water and the other with the sample to be tested, side by side; any yellow or brown colour in the sample indicates the presence of organic matter, but it may not necessarily be owing to very objectionable impurity, since purely vegetable matter, such as peat, may produce it.

The smell can be observed by shaking up some of the water in a large, wide-mouthed flask or bottle, and applying the nose to the bottle immediately afterwards. If the water be warmed to a slight extent, any objectionable smell is more readily detected. The estimation of chlorine, mineral constituents, metals, &c., may be made as described in the foregoing section or by other methods occurring in the previous parts of the book.

PART VII.

VOLUMETRIC ANALYSIS OF GASES.

Description of the necessary Apparatus, with Instructions for Preparing, Etching, Graduating, &c.

§ 86. This branch of chemical analysis, on account of its extreme accuracy, and in consequence of the possibility of its application to the analysis of carbonates, and of many other bodies from which gases may be obtained, deserves more attention than it has generally received, in this country at least. It will, therefore, be advisable to devote some considerable space to the consideration of the subject.

For a historical sketch of the progress of gas analysis, the reader is referred to Dr Frankland's article in the "*Handwörterbuch der Chemie*," and more complete details of the process than it will be necessary to give here will be found in that article, also in Bunsen's "*Gasometry*," and in Dr Russell's contributions to Watt's *Chemical Dictionary*.



Fig. 35.

The apparatus employed by Bunsen, who was the first successfully to work out the processes of gas analysis, is very simple. Two tubes, the absorption tube and the eudiometer, are used, in which the measurement and analysis of the gases are performed. The first of these tubes is about 250 m.m. long and 20 m.m. in diameter, closed at one end, and with a lip at one side of the open extremity, to facilitate the transference of the gas from the absorption tube to the eudiometer (fig. 35). The eudiometer has a length of from 500 to 800 m.m., and a diameter of 20 m.m. Into the closed end two platinum wires are passed,

so as to enable the operator to pass an electric spark through any gas which the tube may contain (fig. 36). The mode of sealing in the platinum wires is as follows:—When the end of the tube is closed, and while still hot, a finely-pointed blowpipe flame is directed against the side of the tube at the base of the hemispherical end. When the glass is soft, a piece of white-hot

platinum wire is pressed against it and rapidly drawn away. By this means a small conical tube is produced. This operation is then repeated on the opposite side (fig. 37). One of the conical tubes is next cut off near to the eudiometer, so as to leave a small orifice (fig. 38), through which a piece of the moderately thin platinum wire, reaching about two-thirds across the tube, is passed. The fine blowpipe flame is now brought to play on the wire at the point where it enters the tube, the glass rapidly fuses round the wire, making a perfectly gas-tight joint. If it should be observed that the tube has any tendency to collapse during the heating, it will be necessary to blow gently into the open end of the tube. This may be conveniently done by means of a long piece of caoutchouc connector, attached to the eudiometer, which enables the operator to watch the effect of the blowing more easily than if the mouth were applied directly to the tube. When a perfect fusion of the glass round the wire has been effected, the point on the opposite side is cut off and a second wire sealed in in the same manner (fig. 39). The end of the tube must be allowed to cool very slowly; if proper attention is not paid to this, fracture is very liable to ensue. When perfectly cold, a piece of wood with a rounded end is passed up the eudiometer, and the two wires carefully pressed against the end of the tube, so as to lie in contact with the glass, with a space of 1 or 2 m.m. between their points (fig. 40). It is for this purpose that the wires, when sealed in, are made to reach so far across the tube. The ends of the wires projecting outside the tube are then bent into loops. These loops must be carefully treated, for if frequently bent they are very apt to break off close to the glass; besides this, the bending of the wire sometimes causes a minute crack in the glass, which may spread and endanger the safety of the tube. These difficulties may be overcome by cutting off the wire close to the glass, and carefully smoothing the ends by rubbing them with a piece of ground glass until they are level with the surface of the tube (fig. 41). In order to make contact with the inductive coil, a wooden American paper clip, lined with platinum foil, is made to grasp the tube; the foil is connected with two strong loops of platinum wire, and to these the wires from the coil



Fig. 36.

are attached (fig. 42). In this way no strain is put on the eudiometer wires by the weight of the wires from the coil, and perfect contact is ensured between the foil and platinum wires. It is also easy to clean the outside of the eudiometer without fear of injuring the instrument.

It will now be necessary to examine if the glass is perfectly

Fig. 37.

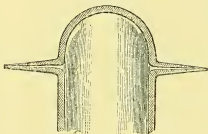


Fig. 38.

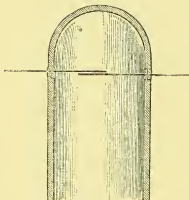
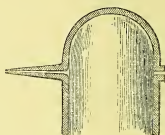


Fig. 39.

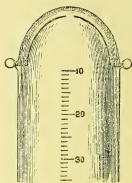


Fig. 40.

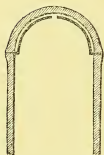


Fig. 41.



Fig. 42.

fused to the wires. For this purpose the eudiometer is filled with mercury, inverted in the trough, the tube held in the hands, and brought with a rapid stroke against the bottom of the trough. This produces a momentary vacuum at the top of the tube; and if there is any leakage, small bubbles will be noticed arising from the junction of the glass with the wires. Of course this experiment must

be carefully performed ; for if the shock is too violent, the mercury, on returning to the top of the tube, may break it.

The tubes are graduated by the following processes :—A cork is fitted into the end of the tube, and a piece of stick, a file, or anything that will make a convenient handle, is thrust into the cork. The tube is heated over a charcoal fire or combustion furnace, and coated with melted wax by means of a camel's hair brush. Sometimes a few drops of turpentine are mixed with the wax to render it less brittle, but this is not always necessary. If, on cooling, it should be found that the layer of wax is not uniform, the tube may be placed in a perpendicular position before a fire and slowly rotated so as to heat it evenly. The wax will then be equally distributed on the surface of the glass, the excess flowing off. The tube must not be raised to too high a temperature, or the wax may become too thin ; but all thick masses should be avoided, as they may prove troublesome in the subsequent operation.

The best and most accurate mode of marking the millimetre divisions on the wax is by a graduating machine, but the more usual process is to copy the graduations from another tube in the following manner.

A hard glass tube, on which millimetre divisions have already been

Fig. 43.

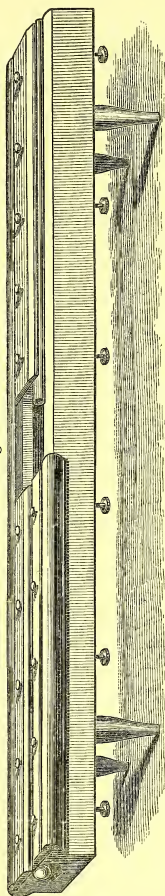


Fig. 44.

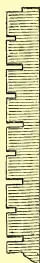


Fig. 45.



deeply etched, is fixed in a groove in the graduating table, a straight edge of brass being screwed down on the tube and covering the ends of the lines. The standard tube is shown in the figure at the right hand end of the apparatus (fig. 43). The waxed tube is secured at the other end of the same groove, and above it are fixed two brass plates, one with a straight edge, and the other with notches at intervals of 5 m.m., the alternate notches being longer than the intermediate ones (fig. 44). A stout rod of wood, provided with a sharp steel point near one end, and a penknife blade at the other (fig. 45), is held so that the steel point rests in one of the divisions of the graduated tube, being gently pressed at the same time against the edge of the brass plate; the point of the knife blade is then moved by the operator's right hand across the portion of the waxed tube which lies exposed between the two brass plates. When the line has been scratched on the wax, the point is moved along the tube until it falls into the next division; another line is now scratched on the wax, and so on. At every fifth division the knife blade will enter the notches in the brass plate, making a longer line on the tube. After a little practice it will be found easy to do fifty or sixty divisions in a minute, and with perfect regularity. Before the tube is removed from the apparatus, it must be carefully examined to see if any mistake has been made. It may have happened that during the graduation the steel point slipped out of one of the divisions in the standard tube; if this has taken place, it will be found that the distance between the line made at that time and those on each side of it will not be equal, or a crooked or double line may have been produced. This is easily obliterated by touching the wax with a piece of heated platinum wire, after which another line is marked. The tube is now taken out of the table, and once more examined. If any portions of wax have been scraped off by the edges of the apparatus, or by the screws, the coating must be repaired with the hot platinum wire. Numbers have next to be marked opposite each tenth division, beginning from the closed end of the tube, the first division, which should be about 10 m.m. from the end, being marked 10 (see fig. 40). The figures may be well made with a steel pen. This has the advantage of producing a double line when the nib is pressed against the tube in making a down stroke. The date, the name of the maker of the tube, or its number, may now be written on the tube.

The etching by gaseous hydrofluoric acid is performed by supporting the tube by two pieces of wire over a long narrow leaden trough

containing sulphuric acid and powdered fluor spar (fig. 46), and the whole covered with a cloth or sheet of paper. Of course it is necessary to leave the cork in the end of the tube to prevent the access of hydrofluoric acid to the interior, which might cause the tube to lose its transparency to a considerable extent. The time required for the action of the gas varies with the kind of glass employed : with ordinary flint glass, from ten minutes to half an hour is quite sufficient ; if the leaden trough is heated the action may take place even still more rapidly. The tube is removed from time to time, and a small portion of the wax scraped off from a part of one of the lines, and if the division can be felt with the finger nail or the point of a knife, the operation is finished ; if not, the wax must be replaced and the tube restored to the trough. When sufficiently etched the tube is washed with water heated before a fire, and the wax wiped off with a warm cloth.

The etching may also be effected with liquid hydrofluoric acid, by applying it to the divisions on the waxed tube with a brush, or by



Fig. 46.

placing the eudiometer in a gutta-percha tube closed at one end and containing some of the liquid.

As all glass tubes are liable to certain irregularities of diameter, it follows that equal lengths of a graduated glass tube will not contain exactly equal volumes. Again, it is, of course, impossible to obtain by measurement of length the capacity of the closed end of the tube.

In order to provide for this, the tube must be carefully calibrated. For this purpose it is supported vertically (fig. 47), and successive quantities of mercury poured in from a measure. This measure should contain about as much mercury as ten or twenty divisions of the eudiometer, and is made of a piece of thick glass tube, closed at one end, and with the edges of the open end ground perfectly flat. The tube is fixed into a piece of wood in order to avoid heating its contents during the manipulation. The measure may be filled with mercury from a vessel closed with a stop-cock terminating in a narrow vertical tube, which is passed to the bottom of the measure (fig. 48). On carefully open

ing the stop-cock the mercury flows into the measure without leaving any air bubbles adhering to the sides. A glass plate is now pressed on the ground edges of the tube, which expels the excess of mercury and leaves the measure entirely filled. The mercury may be introduced into the measure in a manner which is simpler and as effectual, though perhaps not quite so convenient, by first closing it with the glass plate and depressing it in the mercurial trough, removing the plate from the tube, and again replacing it before raising the measure above the surface of the mercury. After pouring each measured quantity of mercury into the eudiometer, the air

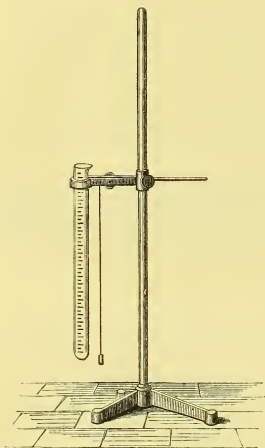


Fig. 47.

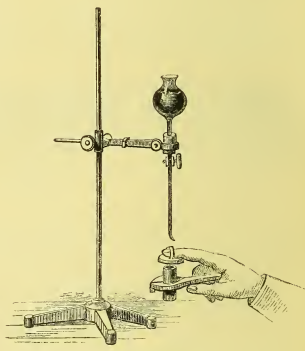


Fig. 48.

bubbles are carefully detached from the sides by means of a thin wooden rod or piece of whalebone, and the level of the mercury at the highest part of the curved surface carefully observed.

In all measurements in gas analysis it is, of course, essential that the eye should be exactly on a level with the surface of the mercury, for the parallax ensuing if this were not the case would produce grave errors in the readings. The placing of the eye in the proper position may be ensured in two ways. A small piece of looking-glass (the back of which is painted, or covered with paper to prevent the accidental soiling of the mercury in the trough), is placed

behind, and in contact with the eudiometer. The head is now placed in such a position that the reflection of the pupil of the eye is precisely on a level with the surface of the mercury in the tube, and the measurement made. As this process necessitates the hand of the operator being placed near the eudiometer, which might cause the warming of the tube, it is preferable to read off with a telescope placed at the distance of from two to six feet from the eudiometer. The telescope is fixed on a stand in a horizontal position, and the support is made to slide on a vertical rod. The image of the surface of the mercury is brought to the centre of the field of the telescope, indicated by the cross wires in the eyepiece, and the reading taken. The telescope has the advantage of magnifying the graduations, and thus facilitating the estimation by the eye of tenths of the divisions (fig. 49).

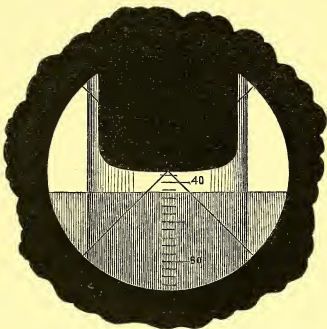


Fig. 49.

By this method the capacity of the tube at different parts of its length is determined. If the tube were of uniform bore, each measure of mercury would occupy the same length in the tube, but as this is never the case, the value of the divisions at all parts of the tube will not be found to be the same.

From the data obtained by measuring the space in the tube which is occupied by equal volumes of mercury, a table is constructed by which the comparative values of each millimetre of the tube can be found. The following results were obtained in the calibration of a short absorption eudiometer :—

On the introduction of the 3d volume of mercury, the reading was 12·8 m.m.

”	”	”	4th	”	”	18·4
”	”	”	5th	”	”	24·0
”	”	”	6th	”	”	29·8
”	”	”	7th	”	”	35·2
”	”	”	8th	”	”	41·0

Thus, the standard volume occupied 5·6 m.m., between 12·8 and 18·4

„	„	5·6	„	„	18·4	„	24·0
„	„	5·8	„	„	24·0	„	29·8
„	„	5·4	„	„	29·8	„	35·2
„	„	5·8	„	„	35·2	„	41·0

If we assume the measure of mercury to contain 5·8 volumes (the greatest difference between two consecutive readings on the tube), the volume at the six points above given will be as follows :—

At 12·8	it will be	17·4	or	5·8	×	3
18·4	„	23·2	„	5·8	×	4
24·0	„	29·0	„	5·8	×	5
29·8	„	34·8	„	5·8	×	6
35·2	„	40·6	„	5·8	×	7
41·0	„	46·4	„	5·8	×	8

Between the first and second readings these 5·8 volumes are contained in 5·6 divisions, consequently each millimetre corresponds to $\frac{5·8}{5·6} = 1·0357$ volumes. This is also the value of the divisions between the second and third readings. Between the third and fourth, 1 m.m. contains 1 vol.; between the fourth and fifth, 1 m.m. contains $\frac{5·8}{5·4} = 1·0741$ vol., and between the fifth and sixth m.m. = 1 vol.

From these data the value of each millimetre on the tube can readily be calculated. Thus 13 will contain the value of 12·8 + the value of 0·2 of a division at this part of the tube, or $17·4 + (1·0357 \times 0·2) = 17·60714$. There is, however, no need to go beyond the second place of decimals, and, for all practical purposes, the first place is sufficient. Thus, by adding or subtracting the necessary volumes from the experimental numbers, we find the values of the divisions nearest to the six points, at which the readings were taken, to be—

13	=	17·61	or	17·6
18	=	22·79	„	22·8
24	=	29·00	„	29·0
30	=	35·00	„	35·0
35	=	40·38	„	40·4
41	=	46·40	„	46·4

In a precisely similar manner the values of the intermediate divisions are calculated, and we thus obtain the following table :—

Readings.	Values.		Readings.	Values.		Readings.	Values.	
10	14.50	14.5	21	25.89	25.9	32	37.15	37.1
11	15.54	15.5	22	26.93	26.9	33	38.22	38.2
12	16.57	16.6	23	27.96	28.0	34	39.30	39.3
13	17.61	17.6	24	29.00	29.0	35	40.38	40.4
14	18.65	18.6	25	30.00	30.0	36	41.40	41.4
15	19.68	19.7	26	31.00	31.0	37	42.40	42.4
16	20.71	20.7	27	32.00	32.0	38	43.40	43.4
17	21.75	21.8	28	33.00	33.0	39	44.40	44.4
18	22.79	22.8	29	34.00	34.0	40	45.40	45.4
19	23.82	23.8	30	35.00	35.0	41	46.40	46.4
20	24.86	24.9	31	36.07	36.1	&c.	&c.	&c.

If it be desired to obtain the capacity of the tube in cubic centimetres, it is only necessary to determine the weight of the quantity of mercury the measure delivers, and the temperature at which the calibration was made, and to calculate the contents by the following formula :—

$$C = \frac{g \times (1 + 0.0001815t)}{13.596 V} .$$

In which g represents the weight of the mercury contained in the measure, t the temperature at which the calibration is made, 0.0001815 being the coefficient of expansion of mercury for each degree centigrade, 13.596 the specific gravity of mercury at 0°C., V the volume read off in the eudiometer, and C the number of cubic centimetres required.

A correction has to be made to every number in the table on account of the surface of the mercury assuming a convex form in the tube. During the calibration, the convexity of the mercury is turned towards the open end of the tube (fig. 50), whilst in the measurement of a gas the convexity will be in the opposite direction (fig. 51). It is obvious that the quantity of mercury measured during the calibration, while the eudiometer is inverted, will be less than a volume of gas contained in the tube when the mercury stands at the same division, while the eudiometer is erect. The necessary amount of correction is determined by observing the position of the top of the meniscus, and then introducing a few drops of

a solution of corrosive sublimate, which will immediately cause the surface of the mercury to become horizontal (fig. 52), and again measuring.

It will be observed that in fig. 50 the top of the meniscus was at the division 39, whereas in fig. 52, after the addition of corrosive sublimate, the horizontal surface of the mercury stands at 38·7, giving a depression of 0·3 m.m. If the tube were now placed erect, and gas introduced so that the top of the meniscus was at 39, and if it were now possible to overcome the capillarity, the horizontal surface would stand at 39·3. The small cylinder of gas between 38·7 and 39·3, or 0·6 divisions, would thus escape measurement. This number 0·6 is therefore called the *error of meniscus*, and must be added to all readings of gas in the eudio-

In these two the mercury should just touch 39.



Fig. 50.



Fig. 51.

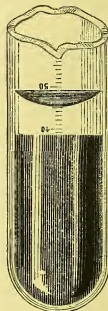


Fig. 52.

meter, so that the difference between the two readings is multiplied by two and the volume represented by the product obtained—the *error of meniscus* is added to the capacities indicated by the table. In the case of the tube, of which the calibration is given above, the difference between the two readings was 0·4 m.m., making the error of meniscus 0·8.

All experiments on gas analysis should be conducted in a room set apart for the purpose, with the window facing the north, so that the sun's rays cannot penetrate into it, and carefully protected from flues or any source of heat which might cause a change of temperature of the atmosphere. The mercury employed should be purified, as far as possible, from lead and tin, which may be done

by leaving it in contact with dilute nitric acid in a shallow vessel for some time, or by keeping it when out of use under concentrated sulphuric acid to which some mercurous sulphate has been added. This mercury reservoir may conveniently be made of a glass globe with a neck at the top and a stopcock at the bottom (fig. 53), and which is not filled more than one-half, so as to maintain as large a surface as possible in contact with the sulphuric acid. Any foreign metals (with the exception of silver, gold, and platinum) which may be present are removed by the mercurous sulphate, an equivalent quantity of mercury being precipitated. This process, which was originated by M. Deville, has been in use for many years with very satisfactory results, the mercury being always clean and dry when drawn from the stopcock at the bottom of the globe. The mouth of the globe should be kept close to prevent the absorption of water by the sulphuric acid.

In all cases, where practicable, gases should be measured when completely saturated with aqueous vapour: to ensure this the top of the eudiometer and absorption tubes should be moistened before the introduction of the mercury. This may be done by dipping the end of a piece of iron wire into water and touching the interior of the closed extremity of the tube with the point of the wire.

In filling the eudiometer, the greatest care must of course be taken to exclude all air-bubbles from the tube. This may be done in several ways: the eudiometer may be held in an inverted or inclined position, and the mercury introduced through a narrow

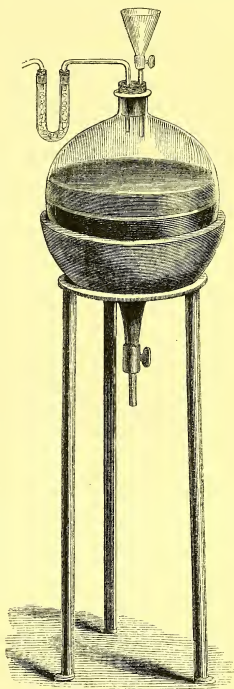


Fig. 53.

glass tube which passes to the end of the eudiometer and communicates, with the intervention of a stopcock, with a reservoir of mercury (fig. 54). On carefully opening the stopcock, the mercury slowly flows into the eudiometer, entirely displacing the air. The same result may be obtained by placing the eudiometer nearly in a horizontal position, and carefully introducing the mercury from a test-tube without a rim (fig. 55). Any minute bubbles adhering to the side may generally be removed by closing the mouth of the tube with the thumb and allowing a small air-bubble to rise in the tube, and thus to wash it out. After filling the eudiometer entirely with mercury, and inverting it over the trough, it will generally be found that the air bubbles have been removed.

For the introduction of the gases, the eudiometer should be placed in a slightly inclined position, being held by a support attached to the mercurial trough (fig. 56), and the gas transferred from the tube

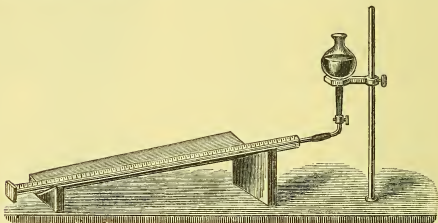


Fig. 54.

in which it has been collected. The eudiometer is now put in an absolutely vertical position, determined by a plumb-line placed near it, and a thermometer suspended in close proximity. It must then be left for at least half-an-hour, no one being allowed to enter the room in the mean time. After the expiration of this period, the operator enters the room, and by means of the telescope placed several feet from the mercury table, carefully observes the height of the mercury in the tube, estimating the tenths of a division with the eye, which can readily be done after a little practice. He next reads the thermometer with the telescope, and finally the height of the mercury in the trough is read off on the tube, for which purpose the trough must have glass sides, the difference between these two numbers being the length of the column of mercury in the eudiometer, and which has to be subtracted from the reading of the barometer. It only remains to take the height of the barometer.

The most convenient form of instrument for gas analysis is the syphon barometer, with the divisions etched on the tube. This is placed on the mercury table, so that it may be read by the telescope immediately after the measurements in the eudiometer. There are two methods of numbering the divisions on the barometer: in one the zero point is at or near the bend of the tube, in which case the height of the lower column must be subtracted from that of the higher; in the other the zero is placed near the middle of the tube, so that the numbers have to be added to obtain the actual height. In cases of extreme accuracy, a correction must be made for the temperature of the barometer, which is determined by a thermometer suspended in the open limb of the instrument, and passing through a plug of cotton wool. Just before observing the height of the barometer, the bulb of the thermometer is depressed for a moment into the mercury in the open limb, thus causing a movement of the mercurial column, which overcomes any tendency that it may have to adhere to the glass.

In every case the volume observed must be reduced to the normal temperature and pressure in order to render the results comparable. If the absolute volume is required, the normal pressure of 760 m.m. must be employed; but when comparative volumes only are desired, the pressure of 1000 m.m. is generally adopted, as it somewhat simplifies the calculation. In the following formula for correction of the volumes of gases:—

V^1 = the corrected volume.

V = the volume found in the table, and corresponding to the observed height of the mercury in the eudiometer, the error of meniscus being of course included.

B = the height of the barometer (corrected for temperature if necessary) at the time of measurement.

b = the difference between the height of the mercury in the trough and in the eudiometer.

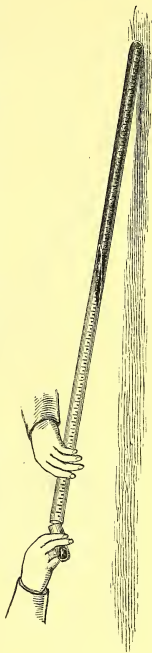


Fig. 55.

t = the temperature in centigrade degrees.

T = the tension of aqueous vapour in millimetres of mercury at t° (see table at end of book). This number is, of course, only employed when the gas is saturated with moisture at the time of measurement.

Then

$$V^1 = \frac{V \times (B - b - T)}{760 \times (1 + 0.003665t)},$$

when the pressure of 760 m.m. is considered the normal one ; or,

$$V, = \frac{V \times (B - b - T)}{1000 \times (1 + 0.003665t)},$$

when the normal pressure of 1 metre is adopted.

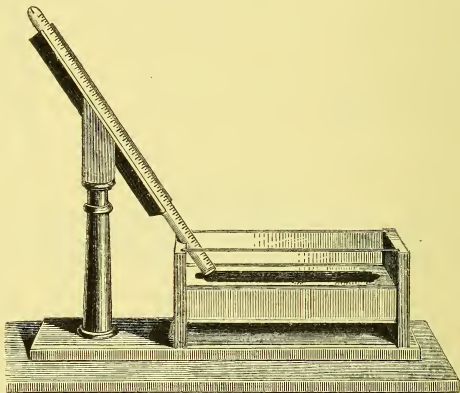


Fig. 56.

In cases where the temperature at measurement is below 0° (which rarely happens), the factor $1 + 0.003665t$ must be placed in the numerator.

Tables have been constructed containing the values of T ; of $1 + 0.003665t$ and of $760 \times (1 + 0.003665t)$, which very much facilitate the numerous calculations required in this branch of analysis (see tables above mentioned).

We shall now be in a position to examine the methods employed in gas analysis. Some gases may be estimated directly ; that is, they may be absorbed by certain re-agents, the diminution of the

volume indicating the quantity of the gas present. Some are determined indirectly; that is, by exploding them with other gases, and measuring the quantities of the products. Some gases may be estimated either directly or indirectly, according to the circumstances under which they are found.

§ 87.

1. GASES ESTIMATED DIRECTLY.**A. Gases Absorbed by Crystallised Sodid Phosphate and Potassic Hydrate :—**

Hydrochloric acid,
Hydrobromic acid,
Hydriodic acid.

B. Gases Absorbed by Potassic Hydrate, and not by Crystallised Sodid Phosphate :—

Carbonic anhydride,
Sulphurous anhydride,
Hydrosulphuric acid.

C. Gases Absorbed by neither Crystallised Sodid Phosphate nor Potassic Hydrate :—

Oxygen,
Nitric oxide,
Carbonic oxide,
Hydrocarbons of the composition C^nH^{2n} ,
Hydrocarbons of the formula $(C^nH^{2n+1})^2$
Hydrocarbons of the formula, C^nH^{2n+2} , except marsh gas.

2. GASES DETERMINED INDIRECTLY.

Hydrogen,
Carbonic oxide,
Marsh gas,
Methyl,
Ethylic hydride,
Ethyl,
Propylic hydride,
Butylic hydride,
Nitrogen.

DIRECT ESTIMATIONS.**Group A, containing Hydrochloric, Hydrobromic, and Hydriodic Acids.**

§ 88. IN Bunsen's method the re-agents for absorption are generally used in the solid form, in the shape of bullets. To make the bullets of sodic phosphate, the end of a piece of platinum wire, of about one foot in length, is coiled up and fixed in the centre of a pistol-bullet mould; it is well to bend the handles of the mould, so that when it is closed the handles are in contact, and may be fastened together by a piece of copper wire (fig. 57). The usual practice is to place the platinum wire in the hole through which the mould is filled; but it is more convenient to file a small notch in one of the faces of the open mould, and place the wire in the notch before the mould is closed. In this manner the wire is not in the way during



Fig. 57.

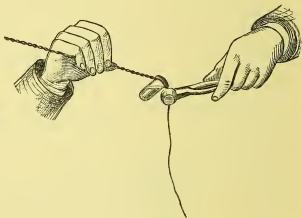


Fig. 58.

the casting, and it is subsequently more easy to trim the bullet. Some ordinary crystallised sodic phosphate is fused in a platinum crucible (or better, in a small piece of wide glass tube, closed at one end and with a spout at the other, and held by a copper wire handle), and poured into the bullet mould (fig. 58). When quite cold, the mould is first gently warmed in a gas flame, opened, and the bullet removed. If the warming of the mould is omitted, the bullet is frequently broken in consequence of its adhering to the metal. Some chemists recommend the use of sodic sulphate instead of phosphate, which may be made into balls by dipping the coiled end of a piece of platinum wire into the salt fused in its water of crystallisation. On removing the wire, a small quantity of the salt will remain attached to the wire. When this has solidified, it is again introduced for a moment and a larger quantity will collect; and this is repeated until the ball

is sufficiently large. The balls must be quite smooth, in order to prevent the introduction of any air into the eudiometer. When the bullets are made in a mould, it is necessary to remove the short cylinder which is produced by the orifice through which the fused salt has been poured.

In the estimation of these gases, it is necessary that they should be perfectly dry. This may be attained by introducing a bullet of fused calcic chloride. After the lapse of about an hour, the bullet may be removed, the absorption-tube placed in a vertical position, with thermometer, &c., arranged for the reading, and left for half-an-hour to assume the temperature of the air. When the reading has been taken, one of the bullets of sodic phosphate or sodic sulphate is depressed in the trough, wiped with the fingers while under the mercury in order to remove any air that it might have carried down with it, and introduced into the absorption-tube, which for this purpose is inclined and held in one hand while the bullet is passed into the tube with the other. Care must be taken that the whole of the platinum wire is covered with mercury while the bullet remains in the gas, otherwise there is a risk of air entering the tube between the mercury and the wire (fig. 59).

After standing for an hour, the bullet is withdrawn from the absorption-tube. This must be done with some precaution, so as to prevent any gas being removed from the tube. It is best done by drawing down the bullet by brisk movement of the wire, the gas being detached from the bullet during the rapid descent of the latter into the mercury. The bullet may then be more slowly removed from the tube. As the sodic phosphate and sodic sulphate owe their absorbent powers for the gases to the water of crystallisation they contain, the bullets must be preserved in a well-closed vessel, and care must be taken that the bullet is not too small for the quantity of gas to be absorbed, as excess of the gas will cause the salt to deliquesce and soil the sides of the eudiometer. When the bullet has been removed, the gas must be dried as before with

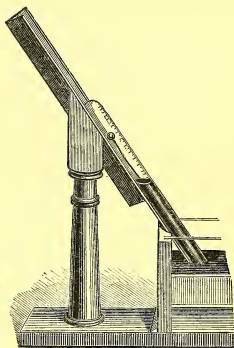


Fig. 59.

calcic chloride and again measured. If two or more of the gases are present in the mixture to be analysed, the sodic phosphate ball must be dissolved in water, and the chlorine, bromine, and iodine determined by the ordinary analytical methods. If this has to be done, care must be taken that the sodic phosphate employed is free from chlorine.

Group B. Gases absorbed by Potassic Hydrate, but not by Sodic Phosphate.

Carbonic anhydride, sulphuretted hydrogen, and sulphurous anhydride.

§ 89. If the gases occur singly, they are determined by means of a bullet of caustic potash made in the same manner as the sodic phosphate balls. The caustic potash employed should contain sufficient water to render the bullets so soft that they may be marked with the nail when cold. Before use the balls must be slightly moistened with water; and if large quantities of gas have to be absorbed, the bullet must be removed after some hours, washed with water, and returned to the absorption-tube. The absorption may extend over twelve or eighteen hours. In order to ascertain if it is completed, the potash ball is removed, washed, again introduced, and allowed to remain in contact with the gas for about an hour. If no diminution of volume is observed the operation is finished.

The following analyses of a mixture of air and carbonic anhydride will serve to show the mode of recording the observations and the methods of calculation required.

Analysis of a Mixture of Air and Carbonic Anhydride.

1. Gas Saturated with Moisture.

Height of mercury in trough	=	171·8 m.m.
Height of mercury in absorption eudiometer	=	89·0 m.m.
Column of mercury in tube, to be subtracted from the height of barometer	= b	<u>82·8 m.m.</u>
Volume in table corresponding to 89 m.m.	=	95·6 m.m.
Correction for error of meniscus	=	<u>0·8 m.m.</u>
Volume of gas	= V	<u>96·4 m.m.</u>

Temperature at which the reading was made	= $t = 12.2^\circ$
Height of barometer at time of observation	= $B = 765.25$ m.m.
Tension of aqueous vapour at 12.2°	= $T = 10.6$ m.m.

$$\begin{aligned}
 V^1 &= \frac{V \times (B - b - T)}{1000 \times (1 + 0.003665t)} = \\
 &= \frac{96.4 + (765.25 - 82.8 - 10.6)}{1000 \times [1 + (0.003665 \times 12.2)]} = \\
 &= \frac{96.4 \times 671.85}{1000 \times 1.044713} = 61.995 \\
 \log. 96.4 &= 1.98408 \\
 \log. 671.85 &= 2.82727 \\
 &= 4.81135 \\
 \log. (1000 \times 1.044713) &= 3.01900 \\
 &= 1.79235 = \log. 61.995 = V^1
 \end{aligned}$$

Corrected volume of air and $\text{CO}^2 = V^1 = 61.995$.

After absorption of carbonic anhydride by bullet of potassic hydrate.

Gas Dry.

Height of mercury in trough	= 172.0 m.m.
Height of mercury in absorption eudiometer	= 62.5 m.m.
Column of mercury in eudiometer	= $b = 109.5$ m.m.
Volume in table corresponding to 62.5 m.m.	= 68.55 m.m.
Correction for error of meniscus	= 0.8 m.m.
Volume of gas	= $V = 69.35$ m.m.
Temperature	= $t = 10.8^\circ$
Barometer	= $B = 766.0$ m.m.

$$\begin{aligned}
 V^1 &= \frac{V \times (B - b)}{1000 \times (1 + 0.003665t)} = \\
 &= \frac{69.35 \times (766.0 - 109.5)}{1000 \times [1 + (0.003665 \times 10.8)]} = \\
 &= \frac{69.35 \times 656.5}{1000 \times 1.039581} = 43.795
 \end{aligned}$$

$$\begin{array}{rcl}
 \log. 69.35 & = & 1.84105 \\
 \log. 656.5 & = & 2.81723 \\
 & & \hline
 & & 4.65828 \\
 \log. (1000 \times 1.039581) & = & 3.01686 \\
 & & \hline
 & & 1.64142 = \log. 43.795 = V^1 \\
 & & \hline
 \end{array}$$

$$\text{Corrected volume of air} = 43.795$$

$$\text{Air} + \text{CO}^2 = 61.995$$

$$\text{Air} = 43.795$$

$$\text{CO}^2 = 18.200$$

$$61.995 : 18.2 :: 100 : x = \text{percentage of CO}^2$$

$$x = \frac{18.2 \times 100}{61.995} = 29.357.$$

$$\text{Percentage of CO}^2 \text{ in mixture of air and gas} = 29.357.$$

2. Gas Moist.

$$\text{Height of mercury in trough,} = 174.0 \text{ m.m.}$$

$$\text{Height of mercury in eudiometer,} = 98.0 \text{ m.m.}$$

$$\text{Column of mercury in tube,} = b = 76.0 \text{ m.m.}$$

$$\text{Volume in table, corresponding to } 98.0 \text{ m.m.} = 104.8 \text{ m.m.}$$

$$\text{Correction for error of meniscus,} = 0.8 \text{ m.m.}$$

$$\text{Volume of gas,} = V = 105.6 \text{ m.m.}$$

$$\text{Temperature,} = t = 12.5^\circ$$

$$\text{Barometer,} = B = 738.0 \text{ m.m.}$$

$$\text{Tension of aqueous vapour at } 12.5^\circ = T = 10.8 \text{ m.m.}$$

$$\text{Corrected volume of air and carbonic anhydride,} = 65.753$$

After absorption of CO^2 .

Gas Dry.

$$\text{Height of mercury in trough,} = 173.0 \text{ m.m.}$$

$$\text{Height of mercury in absorption eudiometer} = 70.3 \text{ m.m.}$$

$$\text{Column of mercury in tube,} = b = 102.7 \text{ m.m.}$$

Volume in table corresponding to 70·3 m.m. = 76·6 m.m.

Correction for error of meniscus, = 0·8 m.m.

Volume of gas, . . . = V = 77·4 m.m.

Temperature, . . . = t = 14·1°

Barometer, . . . = B = 733·5 m.m.

Corrected volume of air, = 46·425

Air + CO² = 65·753

Air = 46·425

CO² = 19·328

65·753 : 19·328 :: 100 : 29·395.

	I.	II.
Percentage of CO ² in mixture of air and gas,	29·357	29·395

If either sulphurous anhydride, or sulphuretted hydrogen occurs together with carbonic anhydride, one of two modes of operation may be followed. Sulphuretted hydrogen and sulphurous anhydride are absorbed by manganic peroxide and by ferric oxide, which may be made into bullets in the following manner. The oxides are made into a paste with water, and introduced into a bullet mould which has been oiled, and containing the coiled end of a piece of platinum wire, the mould is then placed on a sand bath till the ball is dry. The oxides will now be left in a porous condition which would be inadmissible for the purpose to which they are to be applied, the balls are therefore moistened several times with a syrupy solution of phosphoric acid, care being taken that they do not become too soft, so as to render it difficult to introduce them into the eudiometer. After the sulphuretted hydrogen or sulphurous anhydride has been removed, the gas should be dried by means of calcic chloride. The carbonic anhydride can now be determined by means of the bullet of potassic hydrate.

The second method is to absorb the two gases by means of a ball of potassic hydrate containing water, but not moistened on the exterior, then to dissolve the bullet in dilute acetic acid which has been previously boiled and allowed to cool without access of air, and to determine the amount of sulphuretted hydrogen or sulphurous anhydride by means of a standard solution of iodine. This process is especially applicable when rather small quantities of sulphuretted hydrogen have to be estimated.

Group C. This group contains the gases not absorbed by Potassic Hydrate or Sodid Phosphate, and consists of Oxygen, Nitric Oxide, Carbonic Oxide, Hydrocarbons of the formula C^nH^{2n} (C^nH^{2n+1})², and C^nH^{2n+2} , except Marsh gas.

Oxygen was formerly determined by means of a ball of phosphorus, but it is difficult subsequently to free the gas from the phosphorous acid produced, which exerts some tension and so vitiates the results, besides which, the presence of some gases interferes with the absorption of oxygen by phosphorus; and if any potassic hydrate remains on the side of the tube, from the previous absorption of carbonic anhydride, there is a possibility of the formation of phosphoretted hydrogen which would of course vitiate the analysis. A more convenient re-agent is a freshly prepared alkaline solution of potassic pyrogallate introduced into the gas in a bullet of papier maché. The balls of papier maché are made by macerating filter paper in water, and forcing as much of it as possible into a bullet mould into which the end of a piece of platinum wire has been introduced. In order to keep the mould from opening while it is being filled, it is well to tie the handles together with a piece of string or wire, and when charged it is placed on a sand-bath. After the mass is dry the mould may be opened, when a hard absorbent bullet will have been produced. The absorption of oxygen by the alkaline pyrogallate is not very rapid, and it may be necessary to remove the ball once or twice during the operation, and charge it freshly.

Nitric oxide cannot be readily absorbed in an ordinary absorption tube, it may, however, be converted into nitrous anhydride and nitric peroxide by addition of excess of oxygen, absorbing the oxygen compounds with potassic hydrate and the excess of oxygen by potassic pyrogallate. The diminution of the volume will give the quantity of nitric oxide. This process is quite successful when the nitric oxide is mixed with olefiant gas and ethylic hydride, but it is possible that other hydrocarbons might be acted on by the nitrous compounds.

Carbonic oxide may be absorbed by two re-agents. If carbonic anhydride and oxygen be present they must be absorbed in the usual manner, and afterwards a papier maché ball saturated with a concentrated solution of cuprous chloride in dilute hydrochloric acid introduced. A ball of caustic potash is subsequently employed to remove the hydrochloric acid given off by the previous re-agent,

and to dry the gas. Carbonic oxide may also be absorbed by introducing a ball of potassic hydrate, placing the absorption tube in a beaker of mercury, and heating the whole in a water-bath to 100° for 60 hours. The carbonic oxide is thus converted into potassic formate and entirely absorbed.

Olefiant Gas and other Hydrocarbons of the formula C^nH^{2n} , are absorbed by Nordhausen sulphuric acid, to which an additional quantity of sulphuric anhydride has been added. Such an acid may be obtained by heating some Nordhausen acid in a retort connected with a receiver containing a small quantity of the same acid. This liquid is introduced into the gas by means of a dry coke bullet. These bullets are made by filling the mould, into which the usual platinum wire has been placed, with a mixture of equal weights of finely powdered coke and cannel coal. The mould is then heated as rapidly as possible to a bright red heat, and opened after cooling; a hard porous ball is thus produced, which may be employed for many different re-agents. It is sometimes difficult to obtain the proper mixture of coal and coke, but when once prepared, the bullets may be made with the greatest ease and rapidity. The olefiant gas will be absorbed by the sulphuric acid in about an hour, though they may be left in contact for about two hours with advantage. If, on removing the bullet, it still fumes strongly in the air, it may be assumed that the absorption is complete. The gas now contains sulphurous, sulphuric, and perhaps carbonic anhydrides; these may be removed by a manganic peroxide ball, followed by one of potassic hydrate, or the former may be omitted, the caustic potash alone being used. The various members of the C^nH^{2n} group cannot be separated directly, but by the indirect method of analysis their relative quantities in a mixture may be determined.

The hydrocarbons $(C^nH^{2n+1})_2$ and C^nH^{2n+2} , may be absorbed by absolute alcohol, some of which is introduced into the absorption tube, and agitated for a short time with the gas. Correction has then to be made for the weight of the column of alcohol on the surface of the mercury, and for the tension of the alcohol vapour. This method only gives approximate results, and can only be employed in the presence of gases very slightly soluble in alcohol.

The time required in the different processes of absorption just described is considerable, perhaps it might be shortened by surrounding the absorption eudiometer with a wider tube, similar to

the external tube of a Liebig's condenser, and through which a current of water is maintained ; by means of a thermometer in the space between the tubes the temperature of the gas would be known, and the readings might be taken two or three minutes after the withdrawal of the re-agents. Besides this advantage, the great precaution necessary for maintaining a constant temperature in the room might be dispensed with. A few experiments made some years ago in this direction gave satisfactory results.

INDIRECT DETERMINATIONS.

§ 90. GASES which are not absorbed by any re-agents that are applicable in eudiometers over mercury, must be determined in an indirect manner by exploding them with other gases, and noting either the change of volume or the quantity of their products of decomposition, or lastly, as is most frequently the case, by a combination of these two methods. Thus, for example, oxygen may be determined by exploding with excess of hydrogen, and observing the contraction ; hydrogen may be estimated by exploding with excess of oxygen, and measuring the contraction ; and marsh gas by exploding with oxygen, measuring the contraction, and also the quantity of carbonic anhydride generated.

The operation is conducted in the following manner :—The long eudiometer furnished with explosion wires is filled with mercury (after a drop of water has been placed at the top of the tube by means of an iron wire as before described), and some of the gas to be analysed is introduced from the absorption eudiometer. This gas is then measured with the usual precautions, and an excess of oxygen or hydrogen (as the case may be) introduced. These gases may be passed into the eudiometer directly from the apparatus in which they are prepared, or they may be previously collected in lipped tubes of the form of absorption tubes, so as to be always ready for use.

For the preparation of the oxygen, a bulb is used which is blown at the closed end of a piece of combustion tube ; the bulb is about half filled with dry powdered potassic chlorate, the neck drawn out, and bent to form a delivery tube. The chlorate is fused, and the gas allowed to escape for some time to ensure the expulsion of the atmospheric air ; the end of the delivery tube is then brought under the orifice of the eudiometer, and the necessary quantity of gas admitted. When it is desired to prepare the oxygen beforehand, it may be collected directly from the bulb, or, another method to

obtain the gas free from air, may be adopted by those who are provided with the necessary appliances ; this is to connect a bulb containing potassic chlorate with a Sprengel's mercurial air-pump, and after heating the chlorate so as just to fuse it, to produce a vacuum in the apparatus. The chlorate may be again heated until oxygen begins to pass through the mercury at the end of the Sprengel, the heat then withdrawn, and a vacuum once more obtained. The chlorate is once more heated, and the oxygen collected at the bottom of the Sprengel. Of course the usual precautions for obtaining an air-tight joint between the bulb and the Sprengel must be taken, such as surrounding the caoutchouc connector with a tube filled with mercury.

The hydrogen for these experiments must be prepared by electrolysis, since that from other sources is liable to contamination with impurities which would vitiate the analysis. The apparatus employed by Bunsen for this purpose (fig. 60) consists of a glass tube, closed at the lower end, and with a funnel at the other, into which a delivery tube is ground, the funnel acting as a water joint ; a platinum wire is

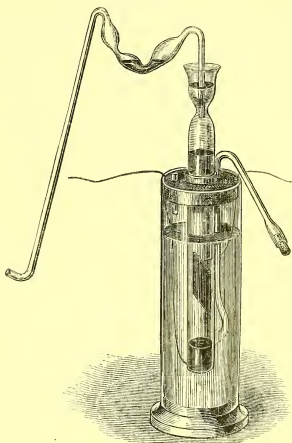


Fig. 60.

sealed into the lower part of the tube, and near the upper end another wire, with a platinum plate attached, is fused into the glass. Some amalgam of zinc is placed into the tube so as to cover the lower platinum wire, and the apparatus filled nearly to the neck with water, acidulated with sulphuric acid. On connecting the platinum wires with a battery of two or three cells, the upper wire being made the negative electrode, pure hydrogen is evolved from the platinum plate, and is dried by passing through the bulbs blown on the delivery-tube, which contains sulphuric acid. After the expulsion of the air, the hydrogen may be at once passed into the eudiometer, or, if preferred, collected in tubes for

future use. Unfortunately, in this form of apparatus, the zinc amalgam soon becomes covered with a saturated solution of zinc sulphate, which puts a stop to the electrolysis. In order to remove this layer, Bunsen has a tube fused into the apparatus just at the surface of the amalgam; this is bent upwards parallel to the larger tube, and curved downwards just below the level of the funnel. The end of the tube is closed with a caoutchouc stopper. On removing the stopper, and pouring fresh acid into the funnel, the saturated liquid is expelled.

Another form of apparatus for preparing electrolytic hydrogen may readily be constructed. A six ounce wide mouth bottle is fitted with a good cork, or better, with a caoutchouc stopper. In the stopper four tubes are fitted (fig. 61): the first is a delivery

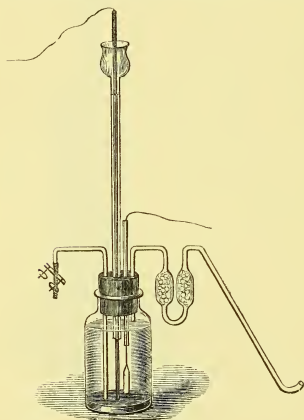


Fig. 61.

acid to conduct the hydrogen to the mercurial trough; the second tube, about 5 centimetres long, and filled with mercury, has fused into its lower end a piece of platinum wire carrying a strip of foil, or the wire may be simply flattened; the third tube passes nearly to the bottom of the bottle, the portion above the cork is bent twice at right angles, and cut off, so that the open end is a little above the level of the shoulder of the bottle, a piece of caoutchouc tube, closed

by a compression cock, is fitted to the end of the tube; the fourth tube is a piece of combustion tube about 30 centimetres in length, and which may with advantage be formed into a funnel at the top. This tube reaches about one-third down the bottle, and inside it is placed a narrower glass tube attached at its lower end by a piece of caoutchouc connector to a rod of amalgamated zinc; the tube is filled with mercury to enable the operator readily to connect the zinc with the battery; some zinc amalgam is placed at the bottom of the bottle, and dilute sulphuric acid is poured in through the wide tube

until the bottle is nearly filled with liquid. To use the apparatus, the delivery tube is dipped into mercury, the wire from the positive pole of the battery placed into the mercury in the tube to which the zinc is attached, and the negative pole connected by means of mercury with the platinum plate. The current, instead of passing between the amalgam at the bottom of the vessel and the platinum plate, as in Bunsen's apparatus, travels from the rod of amalgamated zinc to the platinum, consequently the current continues to pass until nearly the whole of the liquid in the bottle has become saturated with zinc sulphate. As soon as the hydrogen is evolved, of course a column of acid is raised in the funnel until the pressure is sufficient to force the gas through the mercury in which the delivery tube is placed. Care must be taken that the quantity of acid in the bottle is sufficient to prevent escape of gas through the funnel tube, and also that the delivery tube does not pass too deeply into the mercury so as to cause the overflow of the acid. When the acid is exhausted, the compression cock on the bent tube is opened and fresh acid poured into the funnel; the dense zinc sulphate solution is thus replaced by the lighter liquid, and the apparatus is again ready for use.

A very convenient apparatus for transferring oxygen and hydrogen into eudiometers is a gas pipette, figured and described, § 83, page 270.

It is necessary in all cases to add an excess of the oxygen or hydrogen before exploding, and it is well to be able to measure approximately the amount added without going through the whole of the calculations. This may be conveniently done by making a rough calibration of the eudiometer in the following manner:—The tube is filled with mercury, a volume of air introduced into it from a small tube, and the amount of the depression of the mercury noted; a second volume is now passed up, a further depression will be produced, but less in extent than the previous one, in consequence of the shorter column of mercury in the tube; this is repeated until the eudiometer is filled, and by means of a table constructed from these observations, but without taking any notice of the variations of thermometer or barometer, the operator can introduce the requisite quantity of gas. It may be convenient to make this calibration when the eudiometer is inclined in the support, and also when placed perpendicularly, so that the gas may be introduced when the tube is in either position. A table like the following is thus obtained:—

DIVISIONS.

Measures.	Tube Inclined.	Tube Perpendicular.
1	27	45
2	45	69
3	61	87
4	75	102
5	88	116
6	100	128
7	109	138
&c.	&c.	&c.

In explosions of hydrocarbons with oxygen, it is necessary to have a considerable excess of the latter gas in order to moderate the violence of the explosion. The same object may be attained by diluting the gas with atmospheric air, but it is found that sufficient oxygen serves equally well. If the gas contains nitrogen, it is necessary subsequently to explode the residual gas with hydrogen, and if oxygen only has been used for diluting the gas, a very large quantity of hydrogen must be added, which may augment the volume in the eudiometer to an inconvenient extent. When atmospheric air has been employed, this inconvenience is avoided. After the introduction of the oxygen, the eudiometer is restored to its vertical position, allowed to stand for an hour, and the volume read off.

The determination of the quantity of oxygen which must be added to combustible gases so as to prevent the explosion from being too violent, and at the same time to ensure complete combustion, has been made the subject of experiment. When the gases before explosion are under a pressure equal to about half that of the atmosphere, the following proportions of the gases must be employed :—

	Volume of Combustible Gas.	Volume of Oxygen.
Hydrogen,	1	1·5
Carbonic oxide,	1	1·5
Marsh gas,	1	5
Gases containing two atoms of carbon in the molecule, as		
Methyl, C^2H^6 ,	1	10
Gases containing three atoms of carbon in the molecule, as		
Propylic hydride, C^3H^8 ,	1	18
Gases containing four atoms of carbon in the molecule, as		
Ethyl, C^4H^{10} ,	1	25

In cases of mixtures of two or more combustible gases, proportionate quantities of oxygen must be introduced.

At the time of the explosion, it is necessary that the eudiometer should be carefully closed to prevent the loss of gas by the sudden expansion. For this purpose a thick plate of caoutchouc, 3 or 4 centimetres wide, is cemented on a piece of cork by means of marine glue, or some similar substance, and the lower surface of the cork cut so as to lie firmly at the bottom of the mercurial trough (fig. 62). It is, however, preferable to have the caoutchouc permanently fixed in the trough.



Fig 62.

As the mercury does not adhere to the caoutchouc, there is some risk of air entering the eudiometer after the explosion; this is obviated by rubbing the plate with some solution of corrosive sublimate before introducing it into the mercury, which causes the metal to wet the caoutchouc and remove all air from its surface. When the caoutchouc is not fixed in the trough, the treatment with corrosive sublimate has to be repeated before every experiment, and this soils the surface of the mercury to an inconvenient extent. The cushion is next depressed to the bottom of the trough, and the eudiometer placed on it and firmly held down (fig. 63). If this is done with the hands, the tube must be held by that portion containing the mercury, for it is found that when eudiometers burst (which, however, only happens when some precaution has been neglected), they invariably give way just at the level of the mercury within the tube, and serious accidents might occur if the hands were at this point. The

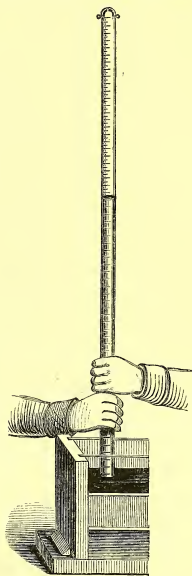


Fig. 63.

cause of the fracture at this point is the following:—Though the gas is at a pressure below that of the atmosphere before the explosion, yet at the instant of the passage of the spark, the expansion of the gas at the top of the tube condenses the layer just below it; this on exploding increases the density of the gas further down

the tube, and by the time the ignition is communicated to the lowest quantity of gas, it may be at a pressure far above that of the atmosphere. It may be thought that the explosion is so instantaneous that this explanation is merely theoretical, but on exploding a long column of gas, the time required for the complete ignition is quite perceptible, and sometimes the flash may be observed to be more brilliant at the surface of the mercury. Some experimenters prefer to fix the eudiometer by means of an arm from a vertical stand, the arm being hollowed out on the under side, and the cavity

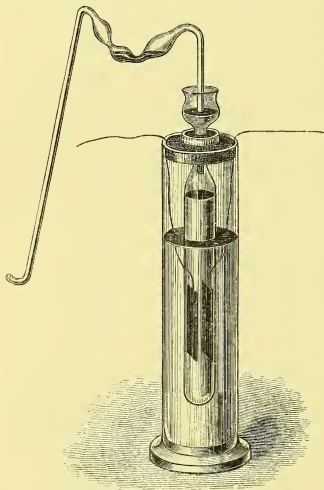


Fig. 64.

lined with cork. If a large quantity of incombustible gas is present, the inflammability of the mixture may be so much reduced that either the explosion does not take place at all, or, what may be worse, only a partial combustion ensues. To obviate this, some explosive mixture of oxygen and hydrogen, obtained by the electrolysis of water, must be introduced. The apparatus used by Bunsen for this purpose is shown in figure 64. The tube in which the electrolysis takes place is surrounded by a cylinder containing

alcohol in order to prevent the heating of the liquid. A convenient apparatus for the preparation of this gas is made by blowing a bulb of about 4 centimetres in diameter on the end of a piece of narrow glass tube, sealing two pieces of flattened platinum wires into opposite sides of the globe, and bending the tube so as to form a delivery tube. Dilute sulphuric acid, containing about 1 volume of acid to 20 of water is introduced into the globe, either before bending the tube, by means of a funnel with a fine and long stem, or, after the bending, by warming the apparatus and plunging the tube into the acid. Care must be taken that the acid is dilute, and that the

battery is not too strong, in order to avoid the formation of ozone, which would attack the mercury, causing the sides of the eudiometer to be soiled, at the same time producing a gas too rich in hydrogen.

The spark necessary to effect the explosion may be obtained from several sources. An ordinary electrical machine or electrophorus may be used, but these are liable to get out of order by damp. Bunsen uses a porcelain tube, which is rubbed with a silk rubber, coated with electrical amalgam; by means of this a small Leyden jar is charged. A still more convenient apparatus is a small induction coil, which will produce a spark of half an inch in length.

After the explosion the eudiometer is slightly raised from the caoutchouc plate to allow the entrance of mercury. When no more mercury rushes in, the tube is removed from the caoutchouc plate, placed in a perpendicular position, and allowed to remain for at least an hour before reading. After measuring the contraction, it is generally necessary to absorb the carbonic anhydride formed by the combustion by means of a potash ball in the way previously described. In some rare instances the amount of water produced in the explosion with oxygen must be measured. If this has to be done, the eudiometer, the mercury, the original gas, and the oxygen, must all be carefully dried. After the explosion the eudiometer is transferred to a circular glass vessel containing mercury, and attached to an iron wire support, by which the entire arrangement can be suspended in a glass tube adapted to the top of an iron boiler, from which a rapid current of steam may be passed through the glass tube so as to heat the eudiometer and mercury to a uniform temperature of 100° . From the measurements obtained at this temperature the amount of water produced may be calculated. If three combustible gases are present, the only data required for calculation are, the original volume of the gas, the contraction on explosion, and the amount of carbonic anhydride generated. When the original gas contains nitrogen, the residue after explosion with excess of oxygen consists of a mixture of oxygen and nitrogen. To this an excess of hydrogen is added, and the mixture exploded; the contraction thus produced divided by 3 gives the amount of oxygen in the residual gas, and the nitrogen is found by difference.

It is obvious that, by subtracting the quantity of residual oxygen, thus determined by explosion with hydrogen, from the amount added, in the first instance, to the combustible gas, the volume of oxygen consumed in the explosion may be obtained. Some chemists

prefer to employ this number instead of the contraction as one of the data for the calculation.

We must now glance at the mode of calculation to be employed for obtaining the percentage composition of a gas from the numbers arrived at by the experimental observations.

The following table shows the relations existing between the volume of the more important combustible gases and the products of the explosion :—

Name of Gas.	Volume of Combustible Gas.	Volume of Oxygen Consumed.	Contraction after Explosion.	Volume of Carbonic Anhydride produced.
Hydrogen, H,	1	0·5	1·5	0
Carbonic Oxide, CO,	1	0·5	0·5	1
Methylic Hydride, CH ³ H,	1	2	2	1
Acetylene, C ² H ² ,	1	2·5	1·5	2
Olefiant Gas, C ² H ⁴ ,	1	3	2	2
Methyl, CH ³ , CH ³ ,	1	3·5	2·5	2
Ethylic Hydride, C ² H ⁵ H,	1	3·5	2·5	2
Propylene, C ³ H ⁶ ,	1	4·5	2·5	3
Propylic Hydride, C ³ H ⁷ H,	1	5	3	3
Butylene, C ⁴ H ⁸ ,	1	6	3	4
Ethyl, C ² H ⁵ , C ² H ⁵ ,	1	6·5	3·5	4
Butylic Hydride, C ⁴ H ⁹ H,	1	6·5	3·5	4

As an example, we may take a mixture of hydrogen, carbonic oxide and marsh gas, which gases may be designated by x , y , and z respectively. The original volume of gas may be represented by A , the contraction by C , and the amount of carbonic anhydride by D .

A will, of course, be made up of the three components, or

$$A = x + y + z.$$

C will be composed as follows : When a mixture of hydrogen and oxygen is exploded, the gas entirely disappears. One volume of hydrogen combining with $\frac{1}{2}$ a volume of oxygen, the contraction will be $1\frac{1}{2}$ times the quantity of hydrogen present, or $1\frac{1}{2}x$. In the case of carbonic oxide, 1 volume of this gas uniting with half its volume of oxygen produces 1 volume of carbonic anhydride, so the contraction due to the carbonic oxide will be $\frac{1}{2}$ its volume, or $\frac{1}{2}y$. Lastly, 1 volume of marsh gas combining with 2 volumes of

oxygen generates 1 volume of carbonic anhydride, so the contraction in this case will be twice its volume, or $2z$. Thus we have—

$$C = 1\frac{1}{2}x + \frac{1}{2}y + 2z.$$

Since carbonic oxide on combustion forms its own volume of carbonic anhydride, the amount produced by the quantity present in the mixture will be y . Marsh gas also generates its own volume of carbonic anhydride, so the quantity corresponding to the marsh gas in the mixture will be z . Therefore

$$D = y + z.$$

It now remains to calculate the values of x , y , and z from the experimental numbers A, C, and D, which is done by the help of the following equations :—

$$\begin{aligned} A &= x + y + z, \\ C &= 1\frac{1}{2}x + \frac{1}{2}y + 2z, \\ D &= y + z. \end{aligned}$$

To find x —

$$\begin{aligned} x + y + z &= A, \\ \frac{y + z}{x} &= \frac{D}{A - D}. \end{aligned}$$

For y we have—

$$\begin{aligned} 4y + 4z &= 4D, \\ \frac{3x + y + 4z}{-3x + 3y} &= \frac{2C}{4D - 2C}, \\ \frac{3x}{3y} &= \frac{3A - 3D}{3A - 2C + D}, \quad \text{or} \\ y &= \frac{3A - 2C + D}{3}. \end{aligned}$$

The value of z is thus found—

$$\begin{aligned} D &= y + z \\ \therefore z &= D - y = \\ D - \frac{3A - 2C + D}{3}, \quad \text{or} \\ z &= \frac{2C - 3A + 2D}{3}. \end{aligned}$$

By replacing the letters A, C, and D by the numbers obtained by experiment, the quantities of the three constituents in the volume A may easily be calculated by the three formulæ :—

$$x = A - D \quad = \text{hydrogen,}$$

$$y = \frac{3A - 2C + D}{3} = \text{carbonic oxide,}$$

$$z = \frac{2C - 3A + 2D}{3} = \text{marsh gas.}$$

The percentage composition is, of course, obtained by the simple proportions—

$$A : x :: 100 : \% \text{ of hydrogen,}$$

$$A : y :: 100 : \% \text{ of carbonic oxide,}$$

$$A : z :: 100 : \% \text{ of marsh gas.}$$

If the gas had contained nitrogen, it would have been determined by exploding the residual gas, after the removal of the carbonic anhydride with excess of hydrogen. The contraction observed, divided by 3, would give the volume of oxygen in the residue, and this, deducted from the residue, would give the amount of nitrogen. If A again represents the original gas, and n the amount of nitrogen it contains, the expression $A - n$ would have to be substituted for A in the above equations.

It may be as well to develop the formula for obtaining the same results by observing the volume of oxygen consumed instead of the contraction. If B represent the quantity of oxygen, we shall have

$$B = \frac{1}{2}x + \frac{1}{2}y + 2z,$$

the values of A and D remaining as before, $x = A - D$.

z is thus found—

$$\begin{aligned} x + y + 4z &= 2B, \\ \frac{x + y + z}{3} &= \frac{A}{3}, \\ 3z &= 2B - A, \text{ or} \\ z &= \frac{2B - A}{3}. \end{aligned}$$

For y —

$$\begin{aligned} D &= y + z \\ \therefore y &= D - z = \\ &= D - \frac{2B - A}{3}, \text{ or} \\ y &= \frac{3D - 2B + A}{3} \end{aligned}$$



Thus we have—

$$\begin{aligned}x &= A - D \\y &= \frac{3D - 2B + A}{3} \\z &= \frac{2B - A}{3}\end{aligned}$$

Having thus shown the mode of calculation of the formulæ, it will be well to give some examples of the formulæ employed in some of the cases which most frequently present themselves in gas analysis.

In all cases—

A = original mixture ,

C = contraction ,

D = carbonic anhydride produced.

1. Hydrogen and Nitrogen.

$$H = x; N = y.$$

Excess of oxygen is added, and the contraction on explosion observed :—

$$\begin{aligned}x &= \frac{2C}{3}, \\y &= \frac{3A - 2C}{3}, \text{ or } A - x.\end{aligned}$$

2. Carbonic Oxide and Nitrogen.

$$CO = x; N = y.$$

The gas is exploded with excess of oxygen, and the amount of carbonic anhydride produced is estimated :—

$$\begin{aligned}x &= D, \\y &= A - D.\end{aligned}$$

3. Hydrogen, Carbonic Oxide, and Nitrogen.

$$H = x; CO = y; N = z.$$

In this case the contraction and the quantity of carbonic anhydride are measured :—

$$\begin{aligned}x &= \frac{2C - D}{3}, \\y &= D, \\z &= \frac{3A - 2C - 2D}{3}.\end{aligned}$$

4. Hydrogen, Marsh Gas, and Nitrogen.

$$H = x; CH^4 = y; N = z.$$

$$x = \frac{2C - 4D}{3},$$

$$y = D,$$

$$z = \frac{3A - 2C + D}{3}.$$

5. Carbonic Oxide, Marsh Gas, and Nitrogen.

$$CO = x; CH^4 = y; N = z.$$

$$x = \frac{4D - 2C}{3},$$

$$y = \frac{2C - D}{3},$$

$$z = A - D.$$

6. Hydrogen, Methyl (or Ethylic Hydride), and Nitrogen.

$$H = x; C^2H^6 = y; N = z.$$

$$x = \frac{4C - 5D}{6},$$

$$y = \frac{D}{2},$$

$$z = \frac{3A - 2C + D}{3}.$$

7. Carbonic Oxide, Methyl (or Ethylic Hydride) and Nitrogen.

$$CO = x; C^2H^6 = y; N = z.$$

$$x = \frac{5D - 4C}{3},$$

$$y = \frac{2C - D}{3},$$

$$z = \frac{3A - 4D + 2C}{3}.$$

8. Hydrogen, Carbonic Oxide, and Marsh Gas.

$$H = x; CO = y; CH^4 = z.$$

$$x = A - D,$$

$$y = \frac{3A - 2C + D}{3},$$

$$z = \frac{2C - 3A + 2D}{3}.$$

9. Hydrogen, Carbonic Oxide, and Ethylic Hydride
(or Methyl).

$$H = x; CO = y; C^2H^6 = z.$$

$$x = \frac{3A + 2C - 4D}{6},$$

$$y = \frac{3A - 2C + D}{3},$$

$$z = \frac{2C - 3A + 2D}{6}.$$

10. Carbonic Oxide, Marsh Gas, and Ethylic Hydride
(or Methyl).

$$CO = x; CH^4 = y; C^2H^6 = z.$$

$$x = \frac{3A - 2C + D}{3},$$

$$y = \frac{3A + 2C - 4D}{3},$$

$$z = D - A.$$

11. Hydrogen, Marsh Gas, and Acetylene.

$$H = x; CH^4 = y; C^2H^2 = z.$$

$$x = \frac{5A - 2C - D}{2},$$

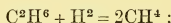
$$y = 2C - 3A,$$

$$z = \frac{D - 2C + 3A}{2}.$$

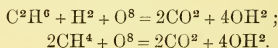
12. Hydrogen, Marsh Gas, and Ethylic Hydride (or Methyl).

$$H = x; CH^4 = y; C^2H^6 = z.$$

This mixture cannot be analysed by indirect determination, since a mixture of two volumes of hydrogen with two volumes of ethylic hydride (or methyl) has the same composition as 4 volumes of marsh gas—



and, consequently, would give rise to the same products on combustion with oxygen as pure marsh gas—



In this case it is necessary to estimate by direct determination the ethylic hydride (or methyl) in a separate portion of the gas by absorption with alcohol, another quantity of the mixture being exploded with oxygen, and the amount of carbonic anhydride produced measured. If the quantity absorbed by alcohol = E, then

$$\begin{aligned} x &= A - D + E, \\ y &= D - 2E, \\ z &= E. \end{aligned}$$

13. Hydrogen, Carbonic Acid, and Propylic Hydride.

$$H = x; CO = y; C^3H^8 = z.$$

$$\begin{aligned} x &= \frac{3A + 4C - 5D}{9}, \\ y &= \frac{3A - 2C + D}{3}, \\ z &= \frac{2C - 3A + 2D}{9}. \end{aligned}$$

14. Carbonic Oxide, Marsh Gas, and Propylic Hydride.

$$CO = x; CH^4 = y; C^3H^8 = z.$$

$$\begin{aligned} x &= \frac{3A - 2C + D}{3}, \\ y &= \frac{3A + 4C - 5D}{6}, \\ z &= \frac{D - A}{2}. \end{aligned}$$

15. Carbonic Oxide, Ethylic Hydride (or Methyl),
and Propylic Hydride.

$$\text{CO} = x; \text{C}^2\text{H}^6 = y; \text{C}^3\text{H}^8 = z.$$

$$x = \frac{3A - 2C + D}{3},$$

$$y = \frac{3A + 4C - 5D}{3},$$

$$z = \frac{4D - 3A - 2C}{3}.$$

16. Marsh Gas, Ethylic Hydride (or Methyl), and
Propylic Hydride.

$$\text{CH}^4 = x; \text{C}^2\text{H}^6 = y; \text{C}^3\text{H}^8 = z.$$

As a mixture of two volumes of marsh gas and two of propylic hydride has the same composition as four of ethylic hydride (or methyl)—

$$\text{CH}^4 + \text{C}^3\text{H}^8 = 2\text{C}^2\text{H}^6,$$

the volume absorbed by alcohol, and which consists of ethylic hydride (or methyl) and propylic hydride, must be determined, and another portion of the gas exploded, and the contraction measured. If E represents the volume absorbed—

$$x = A - E,$$

$$y = 4A - 2C + 2E,$$

$$z = 2C - 4A - E.$$

17. Hydrogen, Carbonic Oxide, and Ethyl (or Butylic
Hydride).

$$\text{H} = x; \text{CO} = y; \text{C}^4\text{H}^{10} = z.$$

$$x = \frac{A + 2C - 2D}{4},$$

$$y = \frac{3A - 2C + D}{3},$$

$$z = \frac{2C + 2D - 3A}{12}.$$

18. Nitrogen, Hydrogen, Carbonic Oxide, Ethylic Hydride (or Methyl), and Butylic Hydride (or Ethyl).

$$N = n; H = w; CO = x; C^2H^6 = y; C^4H^{10} = z.$$

In one portion of the gas the ethylic hydride (or methyl) and the butylic hydride (or ethyl) are absorbed by alcohol; the amount absorbed = E.

A second portion of the original gas is mixed with oxygen and exploded, the amount of contraction and of carbonic anhydride being measured.

The residue now contains the nitrogen and the excess of oxygen, to this an excess of hydrogen is added, the mixture exploded, and the contraction measured. From this the quantity of nitrogen is thus obtained. Let—

$$\begin{aligned} G &= \text{excess of oxygen and nitrogen,} \\ v &= \text{excess of oxygen,} \\ n &= \text{nitrogen,} \\ C' &= \text{contraction on explosion with hydrogen.} \end{aligned}$$

Then—

$$\begin{aligned} G &= v + n, \\ C' &= 3v, \\ 3v &= C', \\ v &= \frac{C'}{3}, \\ n &= G - v = \\ &= G - \frac{C'}{3} = \\ &= \frac{3G - C'}{3}. \end{aligned}$$

From these data the composition of the mixture can be determined—

$$\begin{aligned} w &= \frac{2C - D - 3E}{3}, \\ x &= \frac{3A - 2C + D - 3n}{3}, \\ y &= \frac{3A - 2C - 2D + 12E - 3n}{6}, \\ z &= \frac{2C - 3A + 2D - 6E + 3n}{6}. \end{aligned}$$

MODIFICATIONS AND IMPROVEMENTS UPON THE FOREGOING PROCESSES.

§ 91. In the method of gas analysis that we have been considering, the calculations of results are somewhat lengthy, as will be seen by a reference to the example given of the analysis of a mixture of air and carbonic anhydride (p. 318). Besides this, the operations must be conducted in a room of uniform temperature, and considerable time must be allowed to elapse between the manipulation and the readings in order to allow the eudiometers to acquire the temperature of the surrounding air; and lastly, the absorption of gases by solid re-agents is slow. These disadvantages are to a great extent counterbalanced by the simplicity of the apparatus, and of the manipulation.

From time to time various chemists have proposed methods by which the operations are much hastened and facilitated, and the calculations shortened. It will be necessary to mention a few of these processes, which, however, require special forms of apparatus.

Williamson and Russell have described (*Proceedings of the Royal Society*, vol. ix. p. 218) an apparatus, by means of which the gases in the eudiometers are measured under a constant pressure, the correction for temperature being eliminated by varying the column of mercury in the tube so as to compensate for the alteration of volume observed in a tube containing a standard volume of moist air. In this case solid re-agents were employed in the eudiometers.

In 1864 they published (*Jour. Chem. Soc.*, vol. xvii. 238) a further development of this method, in which the absorptions were conducted in a separate laboratory vessel, by which means the re-agents could be employed in a pasty condition and extended over a large surface.

And in 1868 Dr Russell improved the apparatus, so that liquid re-agents could be used in the eudiometers and the analysis rapidly executed. A description of this last form of instrument is given in the *Journal of the Chemical Society*, vol. xxi. p. 128.

The gutta percha mercury trough employed is provided with a deep well into which the eudiometer can be depressed to any required extent, and on the surface of the mercury a wide glass cylinder, open at both ends and filled with water, is placed. The eudiometer containing the gas to be examined is suspended within the cylinder of water by means of a steel rod passing through a socket attached to a stout standard firmly fixed to the table. In a

similar manner a tube containing moist air is placed by the side of the eudiometer. The clamp supporting this latter tube is provided with two horizontal plates of steel at which the column of the mercury is read off. When a volume of gas has to be measured, the pressure-tube containing the moist air is raised or lowered by means of an ingeniously-contrived fine adjustment until the mercury stands very nearly at the level of one of the horizontal steel plates. The eudiometer is next raised or lowered until the column of mercury within it is at the same level, the final adjustment to bring the top of the meniscus exactly to the lower edge of the steel bar is effected by sliding a closed wide glass tube into the mercury trough. Thus we have two volumes of gas under the same pressure and temperature, and both saturated with moisture; if the temperature of the water in the cylinder increased, there would be a depression of the columns in both tubes, but by lowering the tubes, and thus increasing the pressure until the volume of air in the pressure-tube was the same as before, it would be found that the gas in the eudiometer was restored to the original volume. Again, if the barometric pressure increased, the volumes of the gases would be diminished, but, by raising the tubes to the necessary extent, the previous volumes would be obtained. Therefore, in an analysis, it is only necessary to measure the gas at a pressure equal to that which is necessary to maintain the volume of moist air in the pressure tube constant. The re-agents are introduced into the eudiometer in the liquid state by means of a small syringe made of a piece of glass tube about $\frac{1}{8}$ of an inch in diameter. For this purpose the eudiometer is raised until its open end is just below the surface of the mercury, and the syringe, which is curved upwards at the point, is depressed in the trough, passed below the edge of the water cylinder, and the extremity of the syringe introduced into the eudiometer. When a sufficient quantity of the liquid has been injected, the eudiometer is lowered and again raised so as to moisten the sides of the tube with the liquid, and thus hasten the absorption. Ten minutes was found to be a sufficient time for the absorption of carbonic anhydride when mixed with air.

To remove the liquid re-agent, a ball of moistened cotton wool is employed. The ball is made in the following manner:—A piece of steel wire is bent into a loop at one end, and some cotton wool tightly wrapped round it. It is then dipped in water and squeezed with the hand under the liquid until the air is removed. The end of the steel wire is next passed through a piece of glass tube curved

near one end, and the cotton ball drawn against the curved extremity of the tube. The ball, saturated with water, is now depressed in the mercury trough, and, after as much of the water as possible has been squeezed out of it, it is passed below the eudiometer, and, by pushing the wire, the ball is brought to the surface of the mercury in the eudiometer and rapidly absorbs all the liquid re-agent, leaving the meniscus clean. The ball is removed with a slight jerk, and gas is thus prevented from adhering to it. It is found that this mode of removing the liquid can be used without fear of altering the volume of the gas in the eudiometer.

Carbonic anhydride may be absorbed by a solution of potassic hydrate, and oxygen by means of potassic hydrate and pyrogallie acid. The determination of ethylene is best effected by means of fuming sulphuric acid on a coke ball, water and dilute potassic hydrate being subsequently introduced and removed by the ball of cotton wool.

Doubtless this mode of using the liquid re-agents might be employed with advantage in the ordinary process of analysis to diminish the time necessary for the absorption of the gases. By this process of Dr Russell's the calculations are much shortened and facilitated, the volumes read off being comparable among themselves; this will be seen by an example taken from the original memoir of the determination of oxygen in air—

		Volume in Table corresponding to reading.
Volume of air taken,	130.3	132.15
Volume after absorption of oxygen by potassic hydrate and pyro- gallic acid,	103.5	104.46
	132.15	
	104.46	
	<u>27.69</u>	
volume of oxygen in 132.15 of air.		

132.15 : 27.69 :: 100 : 20.953 percentage of oxygen in air.

Dr Russell has also employed his apparatus for the analysis of carbonates (Journ. Chem. Soc. N. S. vi. 310); for this purpose he adapted a graduated tube, open at both ends, to a glass flask by means of a thick piece of caoutchouc tube. Into the flask, a weighed quantity of a carbonate was placed together with a vessel containing dilute acid. The position of the mercury in the graduated tube was first read off, after which the flask was shaken so as to bring the

acid and carbonate in contact, and the increase of volume was due to the carbonic anhydride evolved. The results thus obtained are extremely concordant.

In eight experiments with sodic carbonate the percentage of carbonic anhydride found varied from 41.484 to 41.607, theory requiring 41.509.

Thirteen experiments with calc spar gave from 43.520 to 43.858, the theoretical percentage being 44.0; and in nine other analyses from 43.581 to 43.901 were obtained.

Two experiments were made with manganic peroxide, oxalic acid and sulphuric acid, and gave 58.156 and 58.101 per cent. of carbonic anhydride.

Some determinations of the purity of magnesium were also performed by dissolving the metal in hydrochloric acid and measuring the resulting hydrogen; four operations gave numbers varying between 8.255 and 8.282; the metal should yield 8.333.

Dr Russell has also employed this process for the determination of the combining proportions of nickel and cobalt (*Journ. Chem. Soc. N. S.*, vii. 294).

MM. Regnault and Reiset described (*Ann. Chim. Phys.* [3] xxvi. 333) an apparatus by which absorptions could be rapidly conducted by means of liquid re-agents brought in contact with the gases in a laboratory tube. The measurements are made in a graduated tube which can be placed in communication with the laboratory tube by means of fine capillary tubes provided with stop cocks, the lower end of the measuring tube being connected by an iron socket and stopcock with another graduated tube in which the pressure, to which the gas is subjected, is measured. The measuring and pressure tubes are surrounded by a cylinder of water. An apparatus similar in principle to this has recently been constructed by Dr Frankland, and is fully described in the section on water analysis, § 83 page 265.

Frankland and Ward (*Chem. Soc. Jour.* vol. vi. p. 197) made several important improvements in the apparatus of Regnault and Reiset. They introduced a third tube (fig. 65), closed at the top with a stopper, and which is made to act as a barometer to indicate the tension of the gas in the measuring tube, thus rendering the operation entirely independent of variations of atmospheric pressure. The correction for aqueous vapour is also eliminated by introducing a drop of water into the barometer as well as into the measuring tube, the pressures produced by the aqueous vapour in

the two tubes thus counterbalancing one another, so that the difference of level of the mercury gives at once the tension of the dry gas. The measuring tube is divided into ten equal divisions (which, for some purposes, require to be calibrated), and in each analysis it is convenient to make all the measurements at the same division, or to calculate the tension which would be exerted by the gas if measured at the tenth division. Frankland and Ward also adapted an iron tube, more than 760 m.m. long, at the bottom of the apparatus, which enables the operator to expand the gas to any required extent, and thus diminish the violence of the explosions which are performed in the measuring tube. During the operation a constant stream of water is kept flowing through the cylinder, which maintains a uniform temperature.

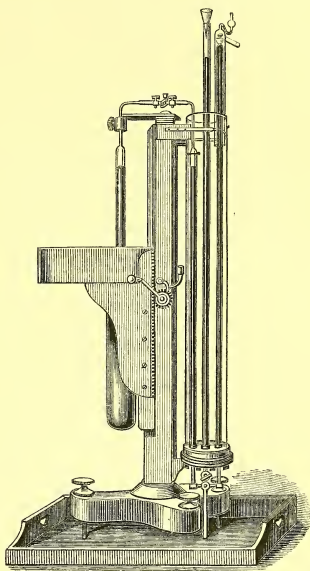


Fig. 65.

By the use of this form of apparatus the calculations of analyses are much simplified; an example of an analysis of atmospheric air will indicate the method of using the instrument:—

Volume of Air used. Determined at 5th Division on the Measuring Tube.

	m.m.
Observed height of mercury in the barometer,	673·0
Height of 5th division,	383·0
Tension of gas,	290·0
	0·5
Corrected tension of gas at 10th division, .	<u>145·00</u>

Volume after Admission of Hydrogen. Determined
at 6th Division,

Observed height of mercury in barometer, .	772.3
Height of 6th division,	304.0
Tension of gas,	<u>468.3</u>
	0.6
Corrected tension at 10th division, . . .	<u>280.98</u>

Volume after Explosion. Determined at 5th Division.

Observed height of mercury in barometer, .	763.3
Height of 5th division,	383.0
Tension of gas,	<u>380.3</u>
	0.5
Corrected tension at 10th division, . . .	<u>190.15</u>
Tension of air with hydrogen.	280.98
Tension of gas after explosion,	<u>190.15</u>
Contraction on explosion,	<u>90.83</u>

of which one-third is oxygen.

$$\frac{90.83}{3} = 30.276 = \text{volumes of oxygen in 145.0 volumes of air}$$

$$145.0 : 30.276 :: 100 : x$$

$$x = \frac{30.276 \times 100}{145.0} = 20.88 = \text{percentage of oxygen in air.}$$

If all the measurements had been made at the same division, no correction to the 10th division would have been necessary, as the numbers would have been comparable among themselves.

Another modification of Frankland and Ward's, or Regnault's apparatus has been described by McLeod (*Journ. Chem. Soc. N. S.* vii. 313), in which the original pressure tube of Regnault's apparatus, or the filling tube of Frankland and Ward, is dispensed with, the mercury being admitted to the apparatus through the stop-cocks at the bottom.

The measuring tube A (fig. 66) is 900 m.m. in length, and about 20 m.m. in internal diameter. It is marked with ten divisions, the first

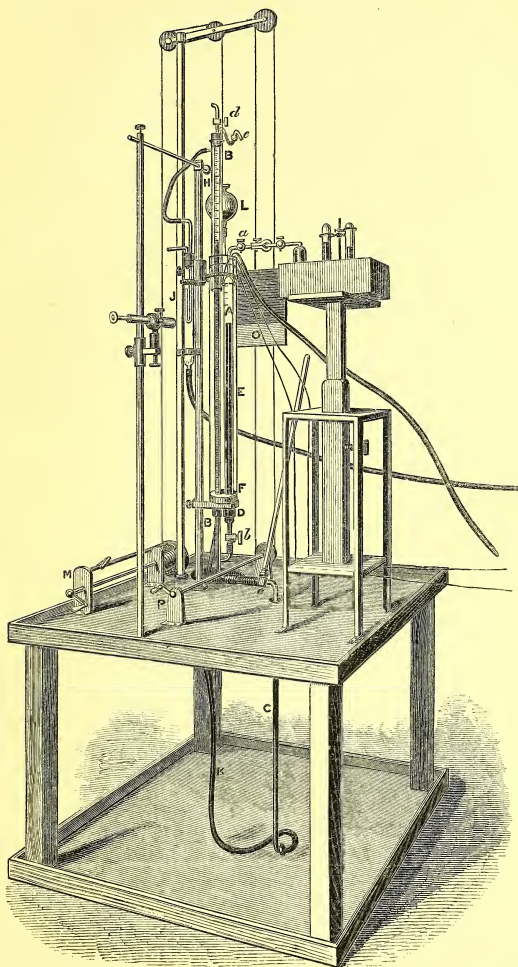


Fig. 66.

at 25 m.m. from the top, the second at 50, the third at 100, and the remaining ones at intervals of 100 m.m. In the upper part of the tube, platinum wires are sealed, and it is terminated by a capillary tube and fine glass stopcock, *a*, the capillary tube being bent at right angles at 50 m.m. above the junction. At the bottom of the tube, a wide glass stopcock *b* is sealed, which communicates, by means of a caoutchouc joint surrounded with tape and well wired to the tubes, with a branch from the barometer-tube B. This latter tube is 5 m.m. in width, and about 1200 m.m. long, and is graduated in millimeters from bottom to top. At the upper extremity a glass stopcock *d* is joined, the lower end being curved and connected by caoutchouc with a stopcock and tube C, descending through the table to a distance of 900 m.m. below the joint. It is advisable to place washers of leather at the end of the plugs of the stopcocks *c* and *b*, as the pressure of the mercury which is afterwards to be introduced has a tendency to force them out; and if this should happen, the washers prevent any great escape of mercury.

The two tubes are firmly held by a clamp D, on which rests a wide cylinder E, about 55 m.m. in diameter, surrounding the tubes, and adapted to them by a water-tight caoutchouc cork F. The cylinder is maintained in an upright position by a support at its upper end G, sliding on the same rod as the clamp. Around the upper part of the barometer-tube a syphon H is fixed by means of a perforated cork, through which the stopcock *d* passes. A small bulb-tube *e*, containing some mercury, is also fitted in this cork, so as to allow of the air being entirely removed from the syphon. The syphon descends about 100 m.m. within the cylinder, and has a branch at the top communicating by caoutchouc with a bent tube contained in a wider one J affixed to the support. A constant current of water is supplied to the cylinder through a glass tube, which passes to the bottom, and escapes through the syphon and tubes to the drain.

To the end of the narrow tube C, is fastened a long piece of caoutchouc tube K, covered with tape, by which a communication is established with the mercurial reservoir L, suspended by a cord, so that by means of the winch M, it may be raised above the level of the top of the barometer-tube. As the mercury frequently forces its way through the pores of the caoutchouc tube, it is advisable to surround the lower part with a piece of wide flexible tube; this

prevents the scattering of the mercury, which collects in a tray placed on the floor. Into the bottom of the tray a screw must be put, to which the end of the glass tube is firmly attached by wire. The capillary stopcock *a* is provided with a steel cap, by means of which it may be adapted to a short and wide laboratory-tube capable of holding about 150 c.c., and identical in form with the one described in the section on Water Analysis (§ 83, p. 265). The mercurial trough for the laboratory-tube is provided with a stand with rings for the purpose of holding two tubes containing gases that may be required.

The apparatus is used in the same way as Frankland and Ward's, except that the mercury is raised and lowered in the tubes by the movement of the reservoir, L, instead of pouring it into the centre supply-tube.

To arrange the apparatus for use, the reservoir L is lowered to the ground, and mercury poured into it. The laboratory-tube being removed, the stopcocks are all opened, and the reservoir gradually raised. When the tube A is filled, the stopcock *a* is closed, and the reservoir elevated until mercury flows through the stopcock *d* at the top of the barometer. It is convenient to have the end of the tube above the stopcock so bent that a vessel can be placed below to receive the mercury. This bend must, of course, be so short that, when the plug of the stopcock is removed, the syphon will pass readily over. When the air is expelled from the barometer-tube, the stopcock is closed. A few drops of water must next be introduced into the barometer; this is accomplished by lowering the reservoir to a short distance below the top of the barometer, and gently opening the stopcock *d*, while a small pipette, from which water is dropping, is held against the orifice, the stopcock being closed when a sufficient amount of water has penetrated into the tube. In the same manner, a small quantity of water is passed into the measuring tube. In order to get rid of any bubbles of air which may still linger in the tubes, the reservoir is lowered to the ground so as to produce a vacuum in the apparatus; in this manner the interior surfaces of the tubes become moistened. The reservoir is now gently raised, thus refilling the tubes with mercury. Great care must be taken that the mercury does not rush suddenly against the tops of the measuring and barometer-tubes, which might cause their destruction; this may be avoided by regulating the flow of mercury by means of the stopcock *c*, which may be conveniently

turned by a long key of wood, resting against the upper table of the sliding stand of the mercurial trough. When the reservoir has again been elevated above the top of the barometer, the stopcocks of the measuring and barometer tubes are opened, and the air and water which have collected allowed to escape.

The heights of the mercurial columns in the barometer corresponding to the different divisions of the measuring tube, have now to be determined. This is done by running out all the mercury from the tubes, and slowly re-admitting it until the meniscus of the mercury just touches the lowest division in the measuring tube. This may be very conveniently managed by observing the division through a small telescope of short focus, and sufficiently close to the apparatus to permit of the key of the stopcock *c* being turned, while the eye is still at the telescope. When a reading is taken, the black screen *O* behind the apparatus must be moved by means of the winch *P*, until its lower edge is about a millimeter above the division. The telescope is now directed to the barometer-tube, and the position of the mercury carefully noted. As the tubes only contain aqueous vapour, and are both at the same temperature, the columns in the two tubes are those which exactly counterbalance one another, and any difference of level that may be noticed is due to capillarity. The same operation is now repeated at each division of the tube. The measuring tube next requires calibration, an operation performed in a manner perfectly similar to that described in the section 82, namely, by filling the measuring tube with water, and weighing the quantities contained between every two divisions. The eudiometer being filled with water, and the stopcock *b* closed, the reservoir is raised and the mercury allowed to rise to the top of the barometer. The capillary stopcock *a* having been opened, the cock *b* is gently turned, and the water allowed to flow out until the mercury reaches the lowest division of the tube. A carefully-weighed flask is now supported just below the steel cap, the stopcock *b* again opened, until the next division is reached, and the quantity of water is weighed, the temperature of the water in the wide cylinder being observed. The same operation is repeated at each division, and by calculation the exact contents of the tube in cubic centimeters may be found.

In this manner a table, such as the following, is obtained :—

Division on measuring tube.	Height of Mercury in Barometer-tube corresponding to division.	Contents.	
		Cubic Centimeters.	Log.
1	756·9	8·6892	0·9389814
2	706·7	18·1621	1·2591664
3	606·8	36·9307	1·5673880
4	506·5	55·7344	1·7461232
5	406·8	74·4299	1·8717477
6	306·8	93·3306	1·9700244
7	206·9	112·4165	2·0508303
8	107·0	131·6335	2·1193666
9	7·1	151·1623	2·1794435

When a gas is to be analysed, the laboratory-tube is filled with mercury, either by sucking the air out through the capillary stopcock, while the open end of the tube stands in the trough, or much more conveniently, by exhausting the air through a piece of flexible tube passed under the mercury to the top of the laboratory-tube, the small quantity of air remaining in the stopcock and at the top of the wide tube being very readily withdrawn. The face of one of the steel pieces is greased with a small quantity of resin cerate, and, the measuring apparatus being full of mercury, the clamp is adjusted.

Before the introduction of the gas, it is advisable to ascertain if the capillary tubes are clear, as a stoppage may arise from the admission of a small quantity of grease into one of them. For this purpose the globe L is raised above the level of the top of the measuring-tube, and the capillary stopcocks opened; if a free passage exists, the mercury will be seen to flow through the tubes. The stopcock of the laboratory-tube is now closed. When all is properly arranged, the gas is transferred into the laboratory-tube, and the stopcock opened, admitting a stream of mercury. The cock *c* is gently turned, so as just to arrest the flow of mercury through the apparatus, and the reservoir lowered to about the level of the table, which is usually sufficient. By carefully opening the cock *c*, the gas is drawn over into the measuring-tube, and when the mercury has reached a point in the capillary-tube of the laboratory tube, about midway between the bend and the stopcock,

the latter is quickly closed. It is necessary that this stopcock should be very perfect. This is attained by grinding the plug into the socket with fine levigated rouge and solution of sodic or potassic hydrate. By this means the plug and socket may be polished so that a very small quantity of resin cerate and a drop of oil renders it perfectly gas-tight. In grinding, care must be taken that the operation is not carried on too long, otherwise the hole in the plug may not coincide with the tubes. If this stopcock is in sufficiently good order, it is unnecessary to close the stopcock *a* during an analysis.

The mercury is allowed to flow out of the apparatus until its surface is a short distance below the division at which the measurements are to be made. The selection of the division depends on the quantity of gas and the kind of experiment to be performed with it. A saving of calculation is effected if all the measurements in one analysis are carried on at the same division. When the mercury has descended below the division, the cock *c* is closed, the reservoir raised, and the black screen moved until its lower edge is about a millimeter above the division, and the telescope placed so that the image of the division coincides with the cross-wires in the eye-piece. The stopcock *c* is now gently opened until the meniscus just touches the division; the cock is closed and the height of the mercury in the barometer is measured by means of the telescope. The difference between the reading of the barometer and the number in the table corresponding to the division at which the measurement is taken, gives in millimetres the tension of the gas. The volume of the gas is found in the same table, and with the temperature, which is read off at the same time as the pressure, all the data required for the calculation of the volume of the gas at 0° and 760 m.m. are obtained. No correction is required for tension of aqueous vapour; the measuring-tube and barometer-tube being both moist, the tensions in the tubes are counterbalanced. Absorptions are performed with liquid re-agents by introducing a few drops of the liquid into the laboratory-tube, transferring the gas into it and allowing the mercury to drop slowly through the gas for about five minutes. The gas is then passed over into the measuring-tube, and the difference of tension observed corresponds to the amount of gas absorbed. It is scarcely necessary to add that the greatest care must be taken to prevent any trace of the re-agent passing the stopcock. If such an accident should occur, the measuring-tube must be washed out several times with distilled water at the con-

clusion of the analysis. If the re-agent is a solution of potassic hydrate it may be got rid of by introducing into the tube some distilled water, to which a drop of sulphuric acid has been added; if this liquid is found to be acid on removing it from the tube, it may be presumed that all the alkali has been neutralised.

When explosions are to be performed in the apparatus, the gas is first measured and then returned to the laboratory-tube. A quantity of oxygen or hydrogen, as the case may be, which is judged to be the proper volume, is transferred into the laboratory-tube, and some mercury is allowed to stream through the gases so as to mix them thoroughly. The mixture is next passed into the eudiometer and measured. If a sufficient quantity of the second gas has not been added, more can readily be introduced. After the measurement, it may be advisable to expand the mixture, in order to diminish the force of the explosion. This is done by allowing mercury to flow out from the tube into the reservoir. When the proper amount of expansion has been reached, the stopcocks *a* and *b* are closed. To enable the electric spark to pass between the wires, it is necessary to lower the level of the water in the cylinder. For this purpose the bent glass tube at the extremity of the syphon is made to slide easily through the cork which closes the top of the wide tube *J*. By depressing the bent tube, the water flows out more rapidly than before, and the level consequently falls. When the surface is below the eudiometer-wires, a spark from an induction-coil is passed, exploding the gas. The syphon tube is immediately raised, and, when the water in the cylinder has reached its original level, the gas is cool enough for measurement. 900 c.c. of mercury are amply sufficient for the whole apparatus; and as there is no cement used to fasten the wide tubes into iron sockets, a great difficulty in the original apparatus is avoided.

The following details of an analysis, in which absorptions only were performed, will show the method employed. The gas was a mixture of nitrogen, oxygen, and carbonic anhydride, and the measurements were all made at division No. 1 on the eudiometer, which had been found to contain 8.6892 c.c.

Original Gas.

Temperature of water in cylinder, 15·4°.

Height of mercury in barometer-tube,	m.m.	980·5
„ „ corresponding to Division No. 1 (see Table),		756·9
Tension of the gas,		<u>223·6</u>

After absorption of the carbonic anhydride by solution of potassic hydrate—

Height of mercury in barometer-tube,		941·7
„ „ corresponding to Division No. 1,		756·9
Tension of the gas after removal of carbonic anhydride,		<u>184·8</u>
Tension of original gas,		223·6
„ gas after removal of carbonic anhydride,		184·8
Tension of carbonic anhydride,		<u>38·8</u>

After absorption of the oxygen by potassic pyrogallate—

Height of mercury in barometer-tube,		885·4
„ „ corresponding to Division No. 1,		756·9
Tension of nitrogen,		<u>128·5</u>
Tension of oxygen and nitrogen,		184·8
„ nitrogen,		128·5
„ oxygen,		<u>56·3</u>

These measurements, therefore, give us the following numbers :—

Tension of nitrogen,	m.m.	128·5
„ oxygen,		56·3
„ carbonic anhydride,		38·8
„ original gas,		<u>223·6</u>

If the percentage composition of the gas is required, it is readily obtained by a simple proportion, the temperature having remained constant during the experiment :—

m.m.	:	m.m.	:	:	100	:	m.m.	per cent.	N
223·6	:	128·5	:	:	100	:	57·469		
223·6	:	56·3	:	:	100	:	25·179	„	O
223·6	:	38·8	:	:	100	:	17·352	„	CO
							<u>100·000</u>		

If, however, it is necessary to calculate the number of cubic centimetres of the gases at 0° and 760 m.m., it is done by the following formulæ:—

$$\frac{8.6892 \times 128.5}{760 \times [1 + (0.003665 \times 15.4)]} = 1.3906 \text{ c.c. of nitrogen.}$$

$$\frac{8.6892 \times 56.3}{760 \times [1 + (0.003665 \times 15.4)]} = 0.6093 \text{ c.c. of oxygen.}$$

$$\frac{8.6892 \times 38.8}{760 \times [1 + (0.003665 \times 15.4)]} = 0.4199 \text{ c.c. of carbonic anhydride.}$$

$$\frac{8.6892 \times 223.6}{760 \times [1 + (0.003665 \times 15.4)]} = 2.4198 \text{ c.c. of the original gas.}$$

If many of these calculations are to be done, they may be very much simplified by constructing a table containing the logarithms of the quotients obtained by dividing the contents of each division of the tube by $760 \times (1 + 0.003665 t)$. The following is a very short extract from such a table:—

T°.	Division No. 1.	Division No. 2.
	Log. $\frac{8.6892}{760 \times (1 + \delta t)}$.	Log. $\frac{18.1621}{760 \times (1 + \delta t)}$.
15.0	$\bar{2}.03492$	$\bar{2}.35511$
.1	$\bar{2}.03477$	$\bar{2}.35496$
.2	$\bar{2}.03462$	$\bar{2}.35481$
.3	$\bar{2}.03447$	$\bar{2}.35466$
.4	$\bar{2}.03432$	$\bar{2}.34451$

By adding the logarithms of the tensions of the gases to those in the above table, the logarithms of the quantities of gases are obtained, thus:—

Log. corresponding to Division No. 1,

and 15.4° , $\bar{2}.03432$

Log. $128.5 =$ tension of nitrogen, . . . $\bar{2}.10890$

Log. of quantity of nitrogen, . . . $\bar{0}.14322$ = log. 1.3906

Volume of nitrogen at 0° and

760 m.m., 1.3906 c.c.

		<u>2.03432</u>	
Log. 56.3 = tension of oxygen, . . .		1.75051	
Log. of quantity of oxygen, . . .		<u>1.78483</u>	= log. 0.6093
Volume of oxygen at 0° and 760 m.m.,		<u>0.6093</u>	c.c.
		<u>2.03432</u>	
Log. 38.8 = tension of carbonic anhy- dride,		1.58883	
Log. of quantity of carbonic anhy- dride,		<u>1.62315</u>	= log. 0.4199
Volume of carbonic anhydride at 0° and 760 m.m.,		<u>0.4199</u>	c.c.
		<u>2.03432</u>	
Log. 223.6 = tension of original gas, . .		2.34947	
Log. of quantity of original gas, . . .		<u>0.38379</u>	= log. 2.4198
Volume of original gas at 0° and 760 m.m.,		<u>2.4198</u>	c.c.
Nitrogen,	1.3906	or	1.391 c.c.
Oxygen,	0.6093	or	0.609 „
Carbonic anhydride,	0.4199	or	0.420 „
Total,	<u>2.4198</u>	or	<u>2.420</u> „

The following example of an analysis of coal gas will show the mode of working with this apparatus, and the various operations to be performed in order to determine the carbonic anhydride, oxygen, hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, marsh gas, carbonic oxide, and nitrogen.

The measuring tube and laboratory tube were first filled with mercury, some of the gas introduced into the laboratory tube, and passed into the apparatus.

The gas was measured at the second division.

Height of mercury in the barometer tube, . .	989.0
„ „ „ measuring tube, . .	<u>706.8</u>
Tension of the gas at 16.6°,	<u>282.2</u>

Two or three drops of a solution of potassic hydrate were now placed in the laboratory tube, and the gas passed from the

measuring tube, the mercury being allowed to drop through the gas for ten minutes. On measuring again—

Height of mercury in barometer,	.	.	.	<u>984.0</u>
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Some saturated solution of pyrogallic acid was introduced into the laboratory tube, and the gas left in contact with the liquid for ten minutes. On measuring—

Height of mercury in barometer,	.	.	.	<u>983.6</u>
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Height of mercury when measuring original gas,				989.0
--	--	--	--	-------

„	„	after absorption of CO ² ,	.	<u>984.0</u>
---	---	---------------------------------------	---	--------------

		Tension of CO ² ,	.	<u>5.0</u>
--	--	------------------------------	---	------------

„	„	after absorption of CO ² ,	.	984.0
---	---	---------------------------------------	---	-------

„	„	after absorption of O,	.	<u>983.6</u>
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		Tension of O,	.	<u>0.4</u>
--	--	---------------	---	------------

The volumes of the gases being proportional to their tensions, it is simple to obtain the percentages of carbonic anhydride and oxygen in the original gas.

Original gas.		CO ²				
282.2	:	5.0	::	100	:	1.772 % CO ²
Original gas.		O				
282.2	:	0.4	::	100	:	0.142 % O
						<u>1.914</u>

By subtracting 1.914 from 100, we obtain the remainder, 98.086, consisting of the hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, carbonic oxide, marsh gas, and nitrogen, thus :—

Original gas,	100.000
O and CO ² ,	<u>1.914</u>
C ⁿ H ²ⁿ . H. CO. CH ⁴ . N.,	<u>98.086</u>

While the gas remains in the measuring tube, the laboratory tube is removed, washed, dried, filled with mercury, and again attached to the apparatus. Much time is saved by replacing the laboratory tube by a second, which was previously ready. As a minute quantity of gas is lost in this operation, in consequence of the amount between the stop-cocks being replaced by mercury, it is advisable to pass the gas into the laboratory tube, then transfer it to the eudiometer, and measure again.

The mixture has now to be exploded, and when the tension is considerable, it is advisable to expand the gas so as to moderate the violence of the explosion. When sufficiently dilated, the stopcock at the bottom of the eudiometer is closed, the level of the water lowered beneath the platinum wires by depressing the syphon, and the spark passed. The explosion should be so powerful that it should be audible, and the flash visible in not too bright daylight.

The stopcock at the bottom of the eudiometer is now opened, and the gas measured.

Height of mercury in barometer after explosion,	<u>732·5</u>
---	--------------

The difference between this reading and the previous one gives the contraction produced by the explosion:—

Height of mercury in barometer before explosion,	789·5
" " " after "	<u>732·5</u>
Contraction = C.,	<u>57·0</u>

It is now necessary to estimate the amount of carbonic anhydride formed. This is done by absorbing with potassic hydrate as before described.

Height of mercury in barometer tube after absorbing CO ² ,	<u>715·8</u>
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This number deducted from the last reading gives the carbonic anhydride.

Height of mercury in barometer after exploding, .	732·5
" " " absorbing CO ² , .	<u>715·8</u>
Carbonic anhydride = D,	<u>16·7</u>

It now remains to determine the quantity of oxygen which was not employed in the explosion, and which excess now exists mingled with the nitrogen. For this purpose a volume of hydrogen about three times as great as that of the residual gas is added, in the same way as the oxygen was previously introduced, and the tension of the mixture determined.

Height of mercury in barometer after adding H,	<u>1031·3</u>
--	---------------

This mixture is exploded and another reading taken.

Height of mercury in barometer after exploding with H,	<u>706·7</u>
--	--------------

This number subtracted from the former, and the difference divided by 3, gives the excess of oxygen.

Height of mercury in barometer before exploding with H,	1031·3
Height of mercury in barometer after exploding with H,	706·7
	3)324·6
Excess of oxygen,	<u>108·2</u>

In order to obtain the quantity of nitrogen in the gas analysed, this number has to be deducted from the volume of gas remaining after the explosion with oxygen and the removal of the carbonic anhydride.

Height of mercury in barometer after absorbing CO ² ,	715·8
„ eudiometer at division No. 3,	606·7
„ Nitrogen and excess of oxygen,	109·1
„ Excess of oxygen,	108·2
„ Nitrogen,	<u>0·9</u>

We have now all the data necessary for the calculation of the composition of the coal gas. It is first requisite to calculate the proportion of the combustible gas present in the coal gas, which is done by deducting the sum of the percentages of gas determined by absorption from 100.

Percentage of carbonic anhydride,	1·772
„ oxygen,	0·142
„ C ⁿ H ²ⁿ ,	4·966
CO ² . O. C ⁿ H ,	<u>6·880</u>
Original gas,	100·000
CO ² . O. C ⁿ H ²ⁿ ,	<u>6·880</u>
H. CO. CH ⁴ . N,	<u>93·120</u>

The formulæ for the calculation of the analysis of a mixture of hydrogen, carbonic oxide, and marsh gas, are (see p. 332).

$$\text{Hydrogen} = x = A - D$$

$$\text{Carbonic oxide} = y = \frac{3A - 2C + D}{3}$$

$$\text{Marsh gas} = z = \frac{2C - 3A + 2D}{3}$$

$$A = 35·5 - 0·9 = 34·6$$

$$C = 57·0$$

$$D = 16·7$$

$$A = 34.6$$

$$D = 16.7$$

$$\underline{\underline{17.9}} = x = \text{hydrogen in 35.5 of the gas exploded with oxygen.}$$

$$A = 34.6$$

$$C = 57.0$$

$$\underline{3}$$

$$\underline{2}$$

$$3A = 103.8$$

$$2C = \underline{\underline{114.0}}$$

$$D = 16.7$$

$$3A + D = 120.5$$

$$2C = 114.0$$

$$3) \underline{6.5} = 3A + D - 2C$$

$$\frac{3A + D - 2C}{3} = \underline{\underline{2.167}} = y = \text{carbonic oxide in 35.5 of the gas.}$$

$$D = 16.7$$

$$\underline{2}$$

$$2D = 33.4$$

$$2C = 114.0$$

$$2D + 2C = 147.4$$

$$3A = 103.8$$

$$3) \underline{43.6} = 2D + 2C - 3A$$

$$\frac{2D + 2C - 3A}{3} = \underline{\underline{14.533}} = z = \text{marsh gas in 35.5 of the gas.}$$

These numbers are readily transformed into percentages, thus :—

$$35.5 : 17.9 :: 93.12 : 46.952\% \text{ of hydrogen.}$$

$$35.5 : 2.167 :: 93.12 : 5.684\% \text{ of carbonic oxide.}$$

$$35.5 : 14.533 :: 93.12 : 38.122\% \text{ of marsh gas.}$$

$$35.5 : 0.9 :: 93.12 : 2.361\% \text{ of nitrogen.}$$

This completes the calculations, the results of which are as follow :—

Hydrogen,	.	.	.	46.952
Marsh gas,	.	.	.	38.122
C^nH^{2n} ,	.	.	.	4.966
Carbonic oxide,	.	.	.	5.684
Carbonic anhydride,	.	.	.	1.772
Oxygen,	.	.	.	0.142
Nitrogen,	.	.	.	2.361
				<u>99.999</u>

It is obvious that this analysis is not quite complete, since it does not give any notion of the composition of the hydrocarbons absorbed by the Nordhausen acid. To determine this, some of the original gas, after the removal of carbonic anhydride and oxygen, is exploded with oxygen, and the contraction and carbonic anhydride produced are measured. The foregoing experiments have shown the effect due to the hydrogen, carbonic oxide, and marsh gas, the excess obtained in the last explosion being obviously caused by the hydrocarbons dissolved by the sulphuric acid, and from these data the composition of the gas may be calculated.

It may be remarked that analyses of this kind were performed with the apparatus at the rate of two a day when working for seven hours.

It may be useful to show how this analysis appears in the laboratory note-book :—

Analysis of Coal Gas.

989.0	} (16.6°) original gas	989.0	984.0
706.8		984.0	983.6
282.2		5.0 = CO ²	0.4 = O
984.0	Aft. absorb. CO ²	282.2 : 5.0 :: 100 : 1.772 CO ²	
		282.2 : 0.4 :: 100 : 0.142 O	
983.6	Aft. absorb. O		1.914
		100.000	
983.3	Remeasured	1.914 CO ² . O	
		98.086 C ⁿ H ²ⁿ . H. CO. CH ⁴ . N	
969.3	Aft. absorb. C ⁿ H ²ⁿ	983.3	983.3
		706.8	969.3
		276.5	14.0 C ⁿ H ²ⁿ
642.2	} Portion of Residue	276.5 : 14.0 :: 98.086 : 4.966 C ⁿ H ²ⁿ .	
606.7			CO ² = 1.772
35.5			O = 0.142
789.5	with O	35.5 = H. CO. CH ⁴ . N	O = 0.142
732.5	Aft. expl.	0.9 = N	C ⁿ H ²ⁿ = 4.966
715.8	Aft. absorb. CO ²	34.6 = H. CO. CH ⁴ = A	6.880
1031.3	with H	789.5	732.5
706.7	Aft. expl.	732.5	715.8
		57.0 = contraction = C	16.7 = CO ² = D
		1031.3	715.8
		706.7	606.7
		324.6	109.1 = N + O
		108.2 = 0	108.2 = O
			0.9 = N

$$\begin{aligned}
 H = x &= A - D &= 17.9 \\
 CO = y &= \frac{3A - 2C + D}{3} &= 2.167 \\
 CH^4 = z &= \frac{2C - 3A + 2D}{3} &= 14.533 \\
 &&34.600 \\
 \hline
 \begin{array}{rcl}
 34.6 &= & A \\
 16.7 &= & D \\
 \hline
 17.9 &= & x = H \\
 \hline
 57.0 &= & C \\
 2 && \\
 \hline
 114.0 &= & 2C
 \end{array}
 \quad
 \begin{array}{rcl}
 34.6 &= & A \\
 3 && \\
 \hline
 103.8 &= & 3A \\
 16.7 &= & D \\
 \hline
 120.5 &= & 3A + D \\
 114.0 &= & 2C \\
 \hline
 6.5 &= & 3A + D - 2C \\
 2.167 &= & y = CO
 \end{array}
 \quad
 \begin{array}{rcl}
 16.7 &= & D \\
 2 && \\
 \hline
 33.4 &= & 2D \\
 114.0 &= & 2C \\
 \hline
 147.4 &= & 2C + 2D \\
 103.8 &= & 3A \\
 \hline
 43.6 &= & 2D - 3A + 2C \\
 14.533 &= & z = CH^4
 \end{array}
 \end{aligned}$$

100.000		35.5 : 17.9 :: 93.12 : 46.952 H
6.880	CO, O, C ⁿ H ²ⁿ	35.5 : 2.167 :: 93.12 : 5.684 CO
93.120	H, CO, CH ⁴ , N	35.5 : 14.533 :: 93.12 : 38.122 CH ⁴
		35.5 : 0.9 :: 93.12 : 2.361 N
	H	= 46.952
	CH ⁴	= 38.122
	C ⁿ H ²ⁿ	= 4.966
	CO	= 5.684
	CO ²	= 1.772
	O	= 0.142
	N	= 2.361
		99.999

Schiebler's Calcimeter, for the Quantitative Estimation of Carbonic Acid in Carbonates, and of the Calcic Carbonate in Bone-Black used for Sugar Refining.

This apparatus is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in bone-black. The principle upon which the apparatus is founded is simply this:—That the quantity of carbonic acid contained in calcic carbonate can, according to well-known rules of combining proportion be used as a measure of the quantity of that salt itself; and instead of determining, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume, and it is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need scarcely possess any knowledge of chemistry. The analytical results obtained by means of this apparatus are

fairly correct, provided care be taken to use all the needful precautions.

The apparatus is shown in fig. 67, and consists of the following parts:—(1.) The glass vessel, A, serves for the decomposition of the

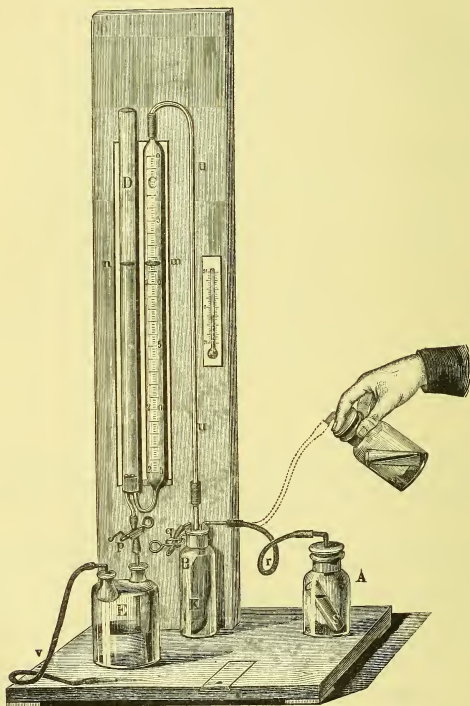


Fig. 67.

material to be tested for carbonic acid, which, for that purpose, is treated with dilute hydrochloric acid; this acid is contained, previous to the beginning of the experiment, in the gutta-percha vessel, *s*. The glass stopper of A is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube, *r*, by means

of which communication is opened with B, a bottle having three openings in its neck. The central opening of this bottle contains a glass tube, *r*, firmly fixed, which is in communication, on the one hand, with A, by means of the flexible india-rubber tube already alluded to, and, on the other hand, *inside* of B, with a very thin india-rubber bladder, K (similar, as regards thinness, to the very light and well-known inflated india-rubber balloons sold as toys). The neck, *q*, of the vessel B is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp; the only use of this opening of the bottle, B, arranged as described, is to give access of atmospheric air to the interior of the bottle, if required. The other opening is in communication with the measuring apparatus, C, a very accurate cylindrical glass tube, of 150 c.c. capacity, divided into 0.5 c.c.; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas; the lower part of this tube D ends in a glass tube of smaller diameter, to which is fastened the india-rubber tube, *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can be readily done by blowing with the mouth into V, and opening the clamp at *p*.

The main portion of the apparatus above described, with the exception, however, of the vessel A, is properly fixed by means of brass fittings to a wooden board, as represented in the woodcut; a thermometer is also attached. The filling of the apparatus with water is very readily effected by pouring it through a suitable funnel placed in the open end of the tube D, care being taken to remove, or at least to unfasten, the spring clamp at *p*; in this manner the water runs into E, which should be almost entirely filled. Distilled water is preferable for this purpose, especially as the filling only requires to be done once, because the water always remains in E as long as the apparatus is intended to be kept ready for use. When it is required to fill the tubes C and D with water, so as to reach the zero of the scale of the instrument, it is best to remove the glass stopper from A. The spring clamp at *p* is next unfastened, and air is then blown by means of the mouth into the tube V, which communicates with E; by this operation the water rises up into the tubes C and D, which thus become filled with that liquid to the

same height. Care should be taken not to force the water up above the zero of the scale at C, and especial care should be taken against forcing so much of the fluid up that it would run over into the tube *u*, and thence find its way to B, whereby a total disconnection of all the parts of the apparatus would become necessary. If by any accident, the water should have been forced up above the zero at C, before the operator had closed the spring clamp at *p*, this is easily remedied by gently opening that clamp, whereby room is given for the water to run off to E in such quantity as may be required to adjust the level of that fluid in C precisely with the zero of the scale. The filling of the tube C with water has the effect of forcing the air previously contained in that tube into B, where it causes the compression of the very thin india-rubber ball placed within B; if it should happen that this india-rubber ball has not become sufficiently compressed and flattened, it is necessary to unfasten the spring clamp at *q*, and to cautiously blow air into B, through the tube *q*, by which operation the complete exhaustion of the india-rubber bladder placed within B is readily performed. This operation is also required only once, because during the subsequent experiments the india-rubber bladder, K, is emptied spontaneously. It may happen, however, that while the filling of the tubes D and C with water is being proceeded with, the india-rubber bladder, K, has become fully exhausted of air before the water in C reaches the zero of the scale; in that case the level of the water in the tubes D and C will not be the same, but will be higher in D; it is evident, however, that this slight defect can be at once remedied by momentarily unfastening the spring clamp at *q*.

The apparatus should be placed so as to be out of reach of direct sunlight, and should also be protected against artificial heat, and all sources of heat which might give rise to sudden changes of temperature; the instrument is best placed near a north window, so as to afford sufficient light for reading off the height of the water in the tubes.

In testing carbonates the method of procedure is as follows:—

Put the very finely powdered portion of carbonate into the perfectly dry decomposing glass A, fill the gutta-percha tube with 10 c.c. hydrochloric acid of 1.12 s.g., place the tube cautiously in the decomposing glass, and then close the bottle with the well-tallowed stopper. Here the water will sink a little in C and rise in D; open *q* for a moment, and the equilibrium will be restored. Now note the thermometer and barometer, grasp the bottle with

the right hand round the neck to avoid warming, raise it, incline it slightly so that the hydrochloric acid may mix with the substance gradually, and at the same time with the left hand regulate p , so that the water in the two tubes may be kept at exactly the same height; continue these operations without intermission till the level of the water in C does not change for a few seconds. Now bring the columns in C and D to exactly the same height, read off the height of the water and note whether the temperature has remained constant. If it has, the number of c.c. read off indicates the liberated carbonic acid; but as a small quantity has been dissolved by the hydrochloric acid, it is necessary to make a correction. Scheibler has determined the small amount of carbonic acid which remains dissolved in the 10 c.c. hydrochloric acid at the mean temperature, and he directs to add 0.8 c.c. to the volume of the carbonic acid read off. Lastly, the volume being reduced to 0° , 760 mm. and the dry condition the weight is found.

If it is desired to dispense with all corrections, each set of experiments may be begun by establishing the relation between the carbonic acid obtained in the process (*i.e.*, the CO^2 actually yielded + 0.8 c.c.) and pure calcic carbonate. This relation is of course dependent on the temperature and pressure prevailing on the particular day. For example, from 0.2737 gm. calcic carbonate containing 0.120428 gm. CO^2 were obtained, 63.8 c.c., including the 0.8 c.c., and in an analysis of dolomite under the same circumstances from 0.2371 gm. substance, were obtained 57.3 c.c., including the 0.8 c.c.

Therefore, $63.8 : 57.3 :: 0.120428 : x$ $x = 0.10816$, consequently the dolomite contains 45.62 per cent. of CO^2 .

For the special procedure in testing bone-black, used in sugar refining, the reader is referred to the printed instructions supplied with the apparatus, or to Mr Crooke's "Treatise on the Manufacture of Beet-root Sugar" (Longmans').

TABLE for Correction of Volumes of Gases for Temperature, according to the Formula $V_t = \frac{V \times B}{760 \times (1 + \delta t)}$
 $1 + \delta t$ from 0° to 30° . $\delta = 0.003665$.

t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$
0.0	1.0000000	0.000 0000	5.0	1.0183250	0.007 8864	10.0	1.0366500	0.015 6321
.1	1.0003665	1591	.1	1.0186915	0.008 0427	.1	1.0370165	7857
.2	1.0007330	3182	.2	1.0190580	1989	.2	1.0373830	9392
.3	1.0010995	4772	.3	1.0194245	4551	.3	1.0377495	0.016 0926
.4	1.0014660	6362	.4	1.0197910	5112	.4	1.0381160	2459
0.5	1.0018325	7951	5.5	1.0201575	6672	10.5	1.0384825	3992
.6	1.0021990	9519	.6	1.0205240	8232	.6	1.0388490	5524
.7	1.0025655	0.001 1127	.7	1.0208905	9791	.7	1.0392155	7056
.8	1.0029320	2714	.8	1.0212570	0.009 1350	.8	1.0395820	8587
.9	1.0032985	4301	5.9	1.0216235	2908	10.9	1.0399485	0.017 0118
1.0	1.0036650	0.001 5888	6.0	1.0219900	0.009 4466	11.0	1.0403150	0.017 1648
.1	1.0040315	7474	.1	1.0223565	6023	.1	1.0406815	3178
.2	1.0043980	9059	.2	1.0227230	7580	.2	1.0410480	4707
.3	1.0047645	0.002 0643	.3	1.0230895	9136	.3	1.0414145	6236
.4	1.0051310	2227	.4	1.0234560	0.010 0692	.4	1.0417810	7764
1.5	1.0054975	3810	6.5	1.0238225	2247	11.5	1.0421475	9292
.6	1.0058640	5393	.6	1.0241890	3802	.6	1.0425140	0.018 0819
.7	1.0062305	6974	.7	1.0245555	5356	.7	1.0428805	2346
.8	1.0065970	8556	.8	1.0249220	6909	.8	1.0432470	3872
1.9	1.0069635	0.003 0137	6.9	1.0252885	8461	11.9	1.0436135	5397
2.0	1.0073300	0.003 1718	7.0	1.0256550	0.011 0013	12.0	1.0439800	0.018 6922
.1	1.0076965	3298	.1	1.0260215	1565	.1	1.0443465	8446
.2	1.0080630	4877	.2	1.0263880	3116	.2	1.0447130	9970
.3	1.0084295	6455	.3	1.0267545	4666	.3	1.0450795	0.019 1493
.4	1.0087960	8033	.4	1.0271210	6216	.4	1.0454460	3016
2.5	1.0091625	9611	7.5	1.0274875	7765	12.5	1.0458125	4538
.6	1.0095290	0.004 1188	.6	1.0278540	9314	.6	1.0461790	6060
.7	1.0098955	2765	.7	1.0282205	0.012 0862	.7	1.0465455	7581
.8	1.0102620	4341	.8	1.0285870	2410	.8	1.0469120	9102
2.9	1.0106285	5916	7.9	1.0289535	3957	12.9	1.0472785	0.020 0622
3.0	1.0109950	0.004 7490	8.0	1.0293200	0.012 5504	13.0	1.0476450	0.020 2141
.1	1.0113615	9063	.1	1.0296865	7050	.1	1.0480115	3660
.2	1.0117280	0.005 0636	.2	1.0300530	8596	.2	1.0483780	5179
.3	1.0120945	2210	.3	1.0304195	0.013 0141	.3	1.0487445	6697
.4	1.0124610	3782	.4	1.0307860	1685	.4	1.0491110	8214
3.5	1.0128275	5354	8.5	1.0311525	3229	13.5	1.0494775	9731
.6	1.0131940	6926	.6	1.0315190	4772	.6	1.0498440	0.021 1248
.7	1.0135605	8497	.7	1.0318855	6315	.7	1.0502105	2764
.8	1.0139270	0.006 0067	.8	1.0322520	7857	.8	1.0505770	4279
3.9	1.0142935	1636	8.9	1.0326185	9399	13.9	1.0509435	5794
4.0	1.0146600	0.006 3205	9.0	1.0329850	0.014 0940	14.0	1.0513100	0.021 7308
.1	1.0150265	4773	.1	1.0333515	2481	.1	1.0516765	8821
.2	1.0153930	6341	.2	1.0337180	4021	.2	1.0520430	0.022 0334
.3	1.0157595	7909	.3	1.0340845	5561	.3	1.0524095	1847
.4	1.0161260	9476	.4	1.0344510	7100	.4	1.0527760	3359
4.5	1.0164925	0.007 1042	9.5	1.0348175	8638	14.5	1.0531425	4871
.6	1.0168590	2607	.6	1.0351840	0.015 0175	.6	1.0535090	6382
.7	1.0172255	4172	.7	1.0355505	1712	.7	1.0538755	7893
.8	1.0175920	5736	.8	1.0359170	3249	.8	1.0542420	9403
4.9	1.0179585	7300	9.9	1.0362835	4785	14.9	1.0546085	0.023 0913

TABLE for Correction of Volumes of Gases—continued.

t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$
		0						
15° 0	1·0549750	·023 2422	20° 0	1·0730000	0·030 7211	25° 0	1·0916250	0·038 0734
·1	1·0553415	3930	·1	1·0736665	8694	·1	1·0919915	2192
·2	1·0557080	5438	·2	1·0740330	0·031 0176	·2	1·0923580	3649
·3	1·0560745	6945	·3	1·0743995	1658	·3	1·0927245	5106
·4	1·0564410	8452	·4	1·0747660	3139	·4	1·0930910	6563
15° 1	1·0568075	9959	20° 1	1·0751325	4620	25° 1	1·0934575	8019
·6	1·0571740	0·024 1465	·6	1·0754990	6100	·6	1·0938240	9474
·7	1·0575405	2970	·7	1·0758655	7580	·7	1·0941905	0·039 0929
·8	1·0579070	4475	·8	1·0762320	9058	·8	1·0945570	2384
15° 9	1·0582735	5979	20° 9	1·0765985	0·032 0538	·9	1·0949235	3838
16° 0	1·0586400	0·024 7483	21° 0	1·0769650	0·032 2016	26° 0	1·0952900	0·039 5291
·1	1·0590065	8986	·1	1·0773315	3493	·1	1·0956565	6744
·2	1·0593730	0·025 0489	·2	1·0776980	4971	·2	1·0960230	8197
·3	1·0597395	1991	·3	1·0780645	6447	·3	1·0963895	9649
·4	1·0601060	3492	·4	1·0784310	7924	·4	1·0967560	0·040 1101
16° 5	1·0604725	4993	21° 5	1·0787975	9399	26° 5	1·0971225	2552
·6	1·0608390	6494	·6	1·0791640	0·033 0874	·6	1·0974890	4003
·7	1·0612055	7994	·7	1·0795305	2349	·7	1·0978555	5453
·8	1·0615720	9494	·8	1·0798970	3824	·8	1·0982220	6902
16° 9	1·0619385	0·026 0993	21° 9	1·0802635	5298	·9	1·0985885	8351
17° 0	1·0623050	0·026 2492	22° 0	1·0806300	0·033 6771	27° 0	1·0989550	0·040 9800
·1	1·0626715	3990	·1	1·0809965	8244	·1	1·0993215	0·041 1248
·2	1·0630380	5488	·2	1·0813630	9716	·2	1·0996880	2696
·3	1·0634045	6985	·3	1·0817295	0·034 1187	·3	1·1000545	4143
·4	1·0637710	8482	·4	1·0820960	2658	·4	1·1004210	5589
17° 5	1·0641375	9978	22° 5	1·0824625	4129	27° 5	1·1007875	7035
·6	1·0645040	0·027 1474	·6	1·0828290	5599	·6	1·1011540	8481
·7	1·0648705	2968	·7	1·0831955	7069	·7	1·1015205	9926
·8	1·0652370	4462	·8	1·0835620	8538	·8	1·1018870	0·042 1371
17° 9	1·0656035	5956	22° 9	1·0839285	0·035 0007	·9	1·1022535	2815
18° 0	1·0659700	0·027 7450	23° 0	1·0842950	0·035 1475	28° 0	1·1026200	0·042 4259
·1	1·0663365	8943	·1	1·0846615	2943	·1	1·1029865	5702
·2	1·0667030	0·028 0435	·2	1·0850280	4410	·2	1·1033530	7145
·3	1·0670695	1927	·3	1·0853945	5877	·3	1·1037195	8587
·4	1·0674360	3418	·4	1·0857610	7343	·4	1·1040860	0·043 0029
18° 5	1·0678025	4909	23° 5	1·0861275	8809	28° 5	1·1044525	1470
·6	1·0681690	6399	·6	1·0864940	0·036 0274	·6	1·1048190	2911
·7	1·0685355	7889	·7	1·0868605	1739	·7	1·1051855	4352
·8	1·0689020	9379	·8	1·0872270	3203	·8	1·1055520	5792
18° 9	1·0692685	0·029 0868	23° 9	1·0875935	4666	·9	1·1059185	7232
19° 0	1·0696350	0·029 2356	24° 0	1·0879600	0·036 6129	29° 0	1·1062850	0·043 8671
·1	1·0700015	3844	·1	1·0883265	7592	·1	1·1066515	0·044 0110
·2	1·0703680	5331	·2	1·0886930	9054	·2	1·1070180	1548
·3	1·0707345	6818	·3	1·0890595	0·037 0516	·3	1·1073845	2986
·4	1·0711010	8304	·4	1·0894260	1978	·4	1·1077510	4423
19° 5	1·0714675	9790	24° 5	1·0897925	3439	29° 5	1·1081175	5859
·6	1·0718340	0·030 1275	·6	1·0901590	4899	·6	1·1084840	7295
·7	1·0722005	2760	·7	1·0905255	6359	·7	1·1088505	8730
·8	1·0725670	4244	·8	1·0908920	7818	·8	1·1092170	0·045 0165
19° 9	1·0729335	5728	·9	1·0912585	9276	·9	1·1095835	1600
						30° 0	1·1099500	0·045 3035

TABLE for Correction of Volumes of Gases for Temperature,
giving the Divisor for the Formula $V' = \frac{V \times B}{760 \times (1 + \delta t)}$.

t	$760 \times (1 + \delta t)$	Log. [760 \times (1 + δt)]	t	$760 \times (1 + \delta t)$	Log. [760 \times (1 + δt)]	t	$760 \times (1 + \delta t)$	Log. [760 \times (1 + δt)]
0.0	760.0000	2.880 8136	4.0	771.1416	2.887 1341	8.0	782.2832	2.893 3640
.1	760.2785	9727	.1	771.4201	2909	.1	782.5617	5186
.2	760.5571	2.881 1318	.2	771.6987	4477	.2	782.8403	6732
.3	760.8356	2908	.3	771.9772	6045	.3	783.1188	8277
.4	761.1142	4498	.4	772.2558	7612	.4	783.3974	9821
0.5	761.3927	6087	4.5	772.5343	9178	8.5	783.6759	2.894 1365
.6	761.6712	7675	.6	772.8128	2.888 0743	.6	783.9544	2908
.7	761.9498	9263	.7	773.0914	2308	.7	784.2330	4451
.8	762.2283	2.882 0850	.8	773.3699	3872	.8	784.5115	5993
.9	762.5069	2437	.9	773.6485	5436	.9	784.7901	7535
1.0	762.7854	2.882 4024	5.0	773.9270	2.888 7000	9.0	785.0686	2.894 9076
.1	763.0639	5610	.1	774.2055	8563	.1	785.3471	2.895 0617
.2	763.3425	7195	.2	774.4841	2.889 0125	.2	785.6257	2157
.3	763.6210	8779	.3	774.7626	1687	.3	785.9042	3697
.4	763.8996	2.883 0363	.4	775.0412	3248	.4	786.1828	5236
1.5	764.1781	1946	5.5	775.3197	4808	9.5	786.4613	6774
.6	764.4566	3528	.6	775.5982	6368	.6	786.7398	8311
.7	764.7352	5111	.7	775.8768	7927	.7	787.0184	9848
.8	765.0137	6692	.8	776.1553	9486	.8	787.2969	2.896 1385
.9	765.2923	8273	.9	776.4339	2.890 1044	.9	787.5755	2921
2.0	765.5708	2.883 9854	6.0	776.7124	2.890 2602	10.0	787.8540	2.896 4457
.1	765.8493	2.884 1434	.1	776.9909	4159	.1	788.1325	5993
.2	766.1279	3013	.2	777.2695	5716	.2	788.4111	7528
.3	766.4064	4591	.3	777.5480	7272	.3	788.6896	9062
.4	766.6850	6169	.4	777.8266	8828	.4	788.9682	2.897 0595
2.5	766.9635	7747	6.5	778.1051	2.891 0383	10.5	789.2467	2128
.6	767.2420	9324	.6	778.3836	1938	.6	789.5252	3660
.7	767.5206	2.885 0901	.7	778.6622	3492	.7	789.8038	5192
.8	767.7991	2477	.8	778.9407	5045	.8	790.0823	6723
.9	768.0777	4052	.9	779.2193	6597	.9	790.3609	8254
3.0	768.3562	2.885 5626	7.0	779.4978	2.891 8149	11.0	790.6394	2.897 9784
.1	768.6347	7199	.1	779.7763	9701	.1	790.9179	2.898 1314
.2	768.9133	8772	.2	778.0549	2.892 1252	.2	791.1965	2843
.3	769.1918	2.886 0345	.3	778.3334	2802	.3	791.4750	4372
.4	769.4704	1918	.4	778.6120	4352	.4	791.7536	5900
3.5	769.7489	3490	7.5	780.8905	5901	11.5	792.0321	7428
.6	770.0274	5062	.6	781.1690	7450	.6	792.3106	8955
.7	770.3060	6633	.7	781.4476	8998	.7	792.5892	2.899 0482
.8	770.5845	8203	.8	781.7261	2.893 0546	.8	792.8677	2008
.9	770.8631	9772	.9	782.0047	2093	.9	793.1463	3533

TABLE for Correction of Volumes of Gases—continued.

t	$760 \times (1 + \delta t)$	Log. $[760 \times (1 + \delta t)]$	t	$760 \times (1 + \delta t)$	Log. $[760 \times (1 + \delta t)]$	t	$760 \times (1 + \delta t)$	Log. $[760 \times (1 + \delta t)]$
12.0	793.4248	2.899 5058	16.5	805.9591	2.906 3129	21.0	818.4934	2.913 0152
1	793.7033	6582	6	806.2376	4630	1	818.7719	1630
2	793.9819	8106	7	806.5162	6130	2	819.0505	3107
3	794.2604	9629	8	806.7947	7630	3	819.3290	4583
4	794.5390	2.900 1152	9	807.0733	9129	4	819.6076	6059
12.5	794.8175	2674	17.0	807.3518	2.907 0628	21.5	819.8861	7535
6	795.0960	4196	1	807.6303	2126	6	820.1646	9010
7	795.3746	5717	2	807.9089	3624	7	820.4432	2.914 0485
8	795.6531	7238	3	808.1874	5121	8	820.7217	1960
9	795.9317	8758	4	808.4660	6618	21.9	821.0003	3434
13.0	796.2102	2.901 0277	17.5	808.7445	8114	22.0	821.2788	2.914 4907
1	796.4887	1796	6	809.0230	9609	1	821.5573	6380
2	796.7673	3315	7	809.3016	2.908 1104	2	821.8359	7852
3	797.0458	4833	8	809.5801	2598	3	822.1144	9323
4	797.3244	6350	9	809.8587	4092	4	822.3930	2.915 0794
13.5	797.6029	7867	18.0	810.1372	2.908 5586	22.5	822.6715	2265
6	797.8814	9384	1	810.4157	7079	6	822.9500	3735
7	798.1600	2.902 0900	2	810.6943	8571	7	823.2286	5205
8	798.4385	2415	3	810.9728	2.909 0063	8	823.5071	6674
9	798.7171	3930	4	811.2514	1554	9	823.7857	8143
14.0	798.9956	2.902 5444	18.5	811.5299	3045	23.0	824.0642	2.915 9611
1	799.2741	6957	6	811.8084	4535	1	824.3427	2.916 1079
2	799.5527	8470	7	812.0870	6025	2	824.6213	2546
3	799.8312	9983	8	812.3655	7515	3	824.8998	4013
4	800.1098	2.903 1495	9	812.6441	9004	4	825.1784	5479
14.5	800.3883	3007	19.0	812.9226	2.910 0492	23.5	825.4569	6945
6	800.6668	4518	1	813.2011	1980	6	825.7354	8410
7	800.9454	6029	2	813.4797	3467	7	826.0140	9875
8	801.2239	7539	3	813.7582	4954	8	826.2925	2.917 1339
9	801.5025	9049	4	814.0368	6440	9	826.5711	2802
15.0	801.7810	2.904 0558	19.5	814.3153	7926	24.0	826.8496	2.917 4265
1	802.0595	2066	6	814.5938	9411	1	827.1281	5728
2	802.3381	3574	7	814.8724	2.911 0896	2	827.4067	7190
3	802.6166	5081	8	815.1500	2380	3	827.6852	8652
4	802.8952	6588	9	815.4295	3864	4	827.9638	2.918 0114
15.5	803.1737	8095	20.0	815.7080	2.911 5347	24.5	828.2423	1575
6	803.4522	9601	1	815.9865	6830	6	828.5208	3035
7	803.7308	2.905 1106	2	816.2651	8312	7	828.7994	4495
8	804.0093	2611	3	816.5436	9794	8	829.0779	5954
9	804.2879	4115	4	816.8222	2.912 1275	24.9	829.3565	7412
16.0	804.5664	2.905 5619	20.5	817.1007	2756	25.0	829.6350	2.918 8870
1	804.8449	7122	6	817.3792	4236	1	829.9135	2.919 0328
2	805.1235	8625	7	817.6578	5716	2	830.1921	1785
3	805.4020	2.906 0127	8	817.9363	7195	3	830.4706	3242
4	805.6806	1628	9	818.2149	8674	4	830.7492	4699

TABLE for Correction of Volumes of Gases—continued.

t	$760 \times$ ($1 + \delta t$).	Log. [760 \times ($1 + \delta t$).	t	$760 \times$ ($1 + \delta t$).	Log. [760 \times ($1 + \delta t$).	t	$760 \times$ ($1 + \delta t$).	Log. [760 \times ($1 + \delta t$).
25.5	831.0277	2.919 6155	27.0	835.2058	2.921 7936	28.5	839.3839	2.923 9606
•6	831.3062	7610	•1	835.4843	9384	•6	839.6624	2.924 1047
•7	831.5848	9065	•2	835.7629	2.922 0832	•7	839.9410	2488
•8	831.8633	2.920 0520	•3	836.0414	2279	•8	840.2195	3928
25.9	832.1419	1974	•4	836.3200	3725	28.9	840.4981	5368
26.0	832.4204	2.920 3427	27.5	836.5985	5171	29.0	840.7766	2.924 6807
•1	832.6989	4880	•6	836.8770	6617	•1	841.0551	8246
•2	832.9775	6333	•7	837.1556	8062	•2	841.3337	9684
•3	833.2560	7785	•8	837.4341	9507	•3	841.6122	2.925 1122
•4	833.5346	9237	27.9	837.7127	2.923 0951	•4	841.8908	2559
26.5	833.8131	2.921 0688	28.0	837.9912	2.923 2395	29.5	842.1693	3995
•6	834.0916	2139	•1	838.2697	3838	•6	842.4478	5431
•7	834.3702	3589	•5	838.5483	5281	•7	842.7264	6866
•8	834.6487	5038	•3	838.8268	6723	•8	843.0049	8301
26.9	834.9273	6487	•4	839.1054	8165	29.9	843.2835	9736
						30.0	843.5620	2.926 1171

**Tension of Aqueous Vapour in Millimetres of Mercury,
from -9° to $+35^{\circ}$ C.**

	m.m.		m.m.		m.m.		m.m.		m.m.		m.m.
-9.9	2.096	-5.4	3.034	-0.9	4.299	3.5	5.889	8.0	8.017	12.5	10.804
8	.114	3	.058	8	.331	6	.930	1	.072	6	.875
7	.132	2	.082	7	.364	7	.972	2	.126	7	.947
6	.150	1	.106	6	.397	8	6.014	3	.181	8	11.019
5	.168	-5.0	.131	5	.430	3.9	.055	4	.236	12.9	.090
-9.4	.186	-4.9	3.156	-0.4	.463	4.0	6.097	8.5	.291	13.0	11.162
3	.204	8	.181	3	.497	1	.140	6	.347	1	.235
2	.223	7	.206	2	.531	2	.183	7	.404	2	.309
1	.243	6	.231	1	.565	3	.226	8	.461	3	.383
-9.0	.261	5	.257	-0.0	4.600	4	.270	8.9	.517	4	.456
-8.9	2.280	-4.4	.283	+0.0	4.600	4.5	.313	9.0	8.574	13.5	.530
8	.299	3	.309	1	.633	6	.357	1	.632	6	.605
7	.318	2	.335	2	.667	7	.401	2	.690	7	.681
6	.337	1	.361	3	.700	8	.445	3	.748	8	.757
5	.356	-4.0	.387	4	.733	4.9	.490	4	.807	13.9	.832
-8.4	.376	-3.9	3.414	0.5	.767	5.0	6.534	9.5	.865	14.0	11.908
3	.396	8	.441	6	.801	1	.580	6	.925	1	.986
2	.416	7	.468	7	.836	2	.625	7	.985	2	12.064
1	.436	6	.495	8	.871	3	.671	8	9.045	3	.142
-8.0	.456	5	.522	0.9	.905	4	.717	9.9	.105	4	.220
-7.9	2.477	-3.4	.550	1.0	4.940	5.5	.763	10.0	9.165	14.5	.298
8	.498	3	.578	1	.975	6	.810	1	.227	6	.378
7	.519	2	.606	2	5.011	7	.857	2	.288	7	.458
6	.540	1	.634	3	.047	8	.904	3	.350	8	.538
5	.561	-3.0	.662	4	.082	5.9	.951	4	.412	14.9	.619
-7.4	.582	-2.9	3.691	1.5	.118	6.0	6.998	10.5	.474	15.0	12.699
3	.603	8	.720	6	.155	1	7.047	6	.537	1	.781
2	.624	7	.749	7	.191	2	.095	7	.601	2	.864
1	.645	6	.778	8	.228	3	.144	8	.665	3	.947
-7.0	.666	5	.807	1.9	.265	4	.193	10.9	.728	4	13.029
-6.9	2.688	-2.4	.836	2.0	5.302	6.5	.242	11.0	9.792	15.5	.112
8	.710	3	.865	1	.340	6	.292	1	.857	6	.197
7	.732	2	.895	2	.378	7	.342	2	.923	7	.281
6	.754	1	.925	3	.416	8	.392	3	.989	8	.366
5	.776	-2.0	.955	4	.454	6.9	.442	4	10.054	15.9	.451
-6.4	.798	-1.9	3.985	2.5	.491	7.0	7.492	11.5	.120	16.0	13.536
3	.821	8	4.016	6	.530	1	.544	6	.187	1	.623
2	.844	7	.047	7	.569	2	.595	7	.255	2	.710
1	.867	6	.078	8	.608	3	.647	8	.322	3	.797
-6.0	.890	5	.109	2.9	.647	4	.699	11.9	.389	4	.885
-5.9	2.914	-1.4	.140	3.0	5.687	7.5	.751	12.0	10.457	16.5	.972
8	.938	3	.171	1	.727	6	.804	1	.526	6	14.062
7	.962	2	.203	2	.767	7	.857	2	.596	7	.151
6	.986	1	.235	3	.807	8	.910	3	.665	8	.241
5	3.010	1.0	.267	4	.848	7.9	.964	4	.734	16.9	.331

	m.m.		m.m.		m.m.		m.m.		m.m.		m.m.		m.m.
17°0	14'421	20°0	17'391	23°0	20'888	26°0	24'988	29°0	29'782	32°0	35'359		
'1	'513	'1	'500	'1	21'016	'1	25'138	'1	'956	'1	'559		
'2	'605	'2	'608	'2	'144	'2	'288	'2	30'131	'2	'760		
'3	'697	'3	'717	'3	'272	'3	'438	'3	'305	'3	'962		
'4	'790	'4	'826	'4	'400	'4	'588	'4	'479	'4	36'165		
17°5	'882	20°5	'935	23°5	'528	26°5	'738	29°5	'654	32°5	'370		
'6	'977	'6	18'047	'6	'659	'6	'891	'6	'833	'6	'576		
'7	15'072	'7	'159	'7	'790	'7	26'045	'7	31'011	'7	'783		
'8	'167	'8	'271	'8	'921	'8	'198	'8	'190	'8	'991		
17°9	'262	20°9	'883	23°9	22'053	26°9	'351	29°9	'369	32°9	37'200		
18°0	15'357	21°0	18'495	24°0	22'184	27°0	26'505	30°0	31'548	33°0	37'410		
'1	'454	'1	'610	'1	'319	'1	'663	'1	'729	'1	'621		
'2	'552	'2	'724	'2	'453	'2	'820	'2	'911	'2	'832		
'3	'650	'3	'839	'3	'588	'3	'978	'3	32'094	'3	38'045		
'4	'747	'4	'954	'4	'723	'4	27'136	'4	'278	'4	'258		
18°5	'845	21°5	19'069	24°5	'858	27°5	'294	30°5	'463	33°5	'473		
'6	'945	'6	'187	'6	'996	'6	'455	'6	'650	'6	'689		
'7	16'045	'7	'305	'7	23'135	'7	'617	'7	'837	'7	'906		
'8	'145	'8	'423	'8	'273	'8	'778	'8	33'026	'8	39'124		
18°9	'246	21°9	'541	24°9	'411	27°9	'939	30°9	'215	33°9	'344		
19°0	16'346	22°0	19'659	25°0	23'550	28°0	28'101	31°0	33'405	34°0	39'565		
'1	'449	'1	'780	'1	'692	'1	'267	'1	'596	'1	'786		
'2	'552	'2	'901	'2	'834	'2	'433	'2	'787	'2	40'007		
'3	'655	'3	20'022	'3	'976	'3	'599	'3	'980	'3	'230		
'4	'758	'4	'143	'4	24'119	'4	'765	'4	34'174	'4	'455		
19°5	'861	22°5	'265	25°5	'261	28°5	'931	31°5	'368	34°5	'680		
'6	'967	'6	'389	'6	'406	'6	29'101	'6	'564	'6	'907		
'7	17'073	'7	'514	'7	'552	'7	'271	'7	'761	'7	41'135		
'8	'179	'8	'639	'8	'697	'8	'441	'8	'959	'8	'364		
19°9	'285	22°9	'763	25°9	'842	28°9	'612	31°9	35'159	34°9	'595		
										35°0	'827		

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£ s. d.

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The same balance in glass case with adjusting screws, 6 6 0
3. Balance with 12-inch beam, to carry 1000 grains in each pan, and turn distinctly with $\frac{1}{80}$ of a grain; the beam is divided; apparatus fixed in case for moving the sliding weight, short pan for taking specific gravities; glass case with adjusting screws. The beam of this balance is constructed with straight knife-edges at the ends, upon which the pans are suspended by agate planes, 8 10 0
- 3a. Above balance with beam, fitted with agate edges and planes, no steel used in construction; front of glass case sliding with counterpoise weights, 10 10 0
4. Balance with 14-inch beam, to carry 1500 grains in each pan, and indicate when loaded $\frac{1}{1000}$ of a grain; the beam is constructed with knife-edges at the ends, upon which the pans are suspended by agate planes; the centre also works upon a single agate plane; the beam is divided; apparatus for moving the sliding weight; pan for taking specific gravities; glass case with adjusting screws, 15 0 0
5. Balance as No. 4, with apparatus for steadying the pans connected with the same axis which moves the beam, so that one movement of the handle first releases the pans, and then the beam; three edges of the beam are made of agate, so that all the working parts of the instrument are most effectually protected against the fumes of the laboratory, or the effects of a damp climate, 18 18 0
6. Balance with 16-inch beam, to carry $1\frac{1}{2}$ lbs to 2 lbs. in each pan, and turn when loaded with $\frac{1}{1000}$ of a grain; the beam is divided; apparatus for moving sliding weight; glass case with adjusting screws, 14 0 0
The same balance with a beam with agate edges, 16 0 0
7. Balance with 16-inch beam, to carry 2 lbs. in each pan, turning with $\frac{1}{1000}$ of a grain, with glass case 10 10 0
- 7a. Balance with 16-inch beam for general use in the laboratory, to carry 2 lbs., turning with half a grain, standing on mahogany board with turned feet 6 6 0

Assay Balances.

8. Balance with 10-inch beam, to carry 500 grains in each pan, turning most distinctly with $\frac{1}{1000}$ of a grain; glass case with adjusting screws, 12 12 0
9. Balance with 8-inch beam to carry 200 grains in each pan, turning most distinctly with $\frac{1}{1000}$ of a grain; the beam is constructed with 3 edges of agate, and the pans are supported by agate planes; apparatus for moving the sliding weight, 18 18 0

	£	s.	d.
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Ditto, ditto, Sodie Chloride,	2/6	8
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Decimal ditto, ditto,	1/6	4/6
„ Solution of Silver, ditto,	2/6	7/6
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Nitrate of Silver,	80/	6/	Platinic Chloride,		30/
Uranic Nitrate,	40/	4/	Ammonic Oxalate,	6/	/6
Uranic Acetate,	40/	4/	Acetic Acid,	2/6	/3
Sodic Hyposulphite,	5/	/6	Citric Acid,	4/	/4
Potassic Ferrocyanide,	5/	/6	Tartaric Acid,	4/	/4
Potassic Ferridcyanide,	8/	/8	Ammonic Chloride,	5/	/6
Baric Chloride,	5/	/6	Ferric Chloride, Solution,	5/	/6
Sodic Chloride,	5/	/6	Potassic Cyanide,	21/	1/6
Iodine,	36/	3/6	Metallic Silver,	128/	10/
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Sodic Phosphate,	5/	/6	Potassic Chromate,	6/	/6
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